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Thermo-Oxidative Behavior of PTMG and PPG Based Polyurethane-Ureas With Varying Degree of Fluorination

Rogerio Silva Tocchetto
University of Tennessee - Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Rogerio Silva Tocchetto entitled "Thermo-Oxidative Behavior of PTMG and PPG Based Polyurethane-Ureas With Varying Degree of Fluorination." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

Roberto S. Benson, Major Professor

We have read this thesis and recommend its acceptance:

Kevin Kit, Raymond Buchanan

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Vice Provost and
Dean of Graduate Studies

(Original Signatures are on file in the Graduate Student Services Office)

Thermo-Oxidative Behavior of PTMG and PPG Based Polyurethane-Ureas With Varying Degree of Fluorination

A Thesis

Presented for the

Masters of Science Degree

The University of Tennessee Knoxville

Rogério Silva Tocchetto

December 2002

Dedication

This work is dedicated to my family.

"A long way, but inspiration is all we're looking for."

Acknowledgements

I want to show my appreciation for the help of those that contributed, for the development of this study. First of all, Thank you Dr. Benson for your great support and guidance thorough all steps of this study and on my educational process, you made it possible. I also am very grateful for the help of my committee members Dr. Kit and Dr. Buchanan, who made great contributions for this research.

My appreciation is extended to my friends and colleagues that were part of this special period of my life. Thank you Xiaoyu Luo, George Jacob, Chris Stephen, Chris Lewis.

Thank you Dr. Hyung-Joong Kim for providing the unique polymers used on this research, your work made mine feasible.

I want to express my sincere appreciation for the Materials Science and Engineering department for the investment in my education.

Finally, I want to express my special appreciation for the unconditional love and support of my parents and wife, whose generosity and attention are the energy for my accomplishments.

Abstract

The thermo-oxidative behavior of ether based fluorinated polyurethane elastomers was assessed. For achieving this goal, samples were exposed to high temperatures (118±3°C) for periods of up to eight weeks. The chemical structure changes were monitored through infrared spectroscopy and several other test methods such as mass retention, contact angle measurements and viscosity measurements. Thermo-gravimetric analysis was done for the unexposed samples, and the mechanical properties of these materials were monitored through a multi-frequency dynamic mechanical analyzer.

The polyurethanes supplied for this study are ether based polymers synthesized in a two step process where on the first step 4,4'-diphenyl methane diisocyanate (MDI) was coupled with polytetramethylene glycol (PTMG) or with polypropylene glycol (PPG) to form a pre-polymer. For the fluorinated polymers, this first step included a third component. This component is a perfluoro polyether diol (Mn=2000) and its proportion to the basic glycols defined the percentage of fluorination of the final polymer. On the second step, ethylene diamine (EDA) was used as a chain extender to generate polymers with molecular weight in the range of 130,000 (50% fluorinated) to M_W 287,000 (0% fluorinated).

Results show that the presence of fluorinated groups changes the dynamics of the degradation process and it results in better thermo-oxidative resistance as well as better mechanical properties retention along the exposure times and poorer surface wettability, appreciable for most surface treatment applications. The fluorination of these polymers via substitutions of the polyglycol on the first step of polymerization accentuates some thermo-oxidative effects on the base polyurethanes, such as mass retention with exposure and yellowing, what could be attributed to smaller chain lengths of the fluorinated segments.

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List of Abbreviations

A	Absorbance
ATR	Attenuated total reflectance
BTD	1,4 butane diol
C	Solution concentration
DMA	Dynamic mechanical analysis
DMF	N,N-dimethyformamide
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
E’	Storage modulus
E”	Loss modulus
E_{coh}	Cohesive energy
EDA	Ethylene diamine
F	Fomblin Z-DOL 2000 ®
FPUE	Fluorinated polyurethane elastomer
FT-IR	Fourier transform infrared analysis
HDPE	High density polyethylene
IR	Infrared
K	Proportionality constant for infrared
M and E	Electric field vectors
MDI	4,4’-Diphenyl methane diisocyanate
MW	Molecular weight
NMR	Nuclear magnetic resonance
PA 6,6	Plyamide 6,6 (Nylon 66®)
PE	Polyethylene
PEOG	Polyethylene oxide glycol
PPG	Polypropylene glycol
PTFE	Poly(tetrafluoro ethylene)
PTMG	Polytetramethylene glycol

PTMO	Poly(tetramethylene oxide)
PU	Polyurethane
PUE	Polyurethane elastomer
PVC	Poly vinyl chloride
t	Efflux time
TDI	2,4-diisocyanate
Tg	Glass transition temperature
TGA	Thermal gravimetric analysis
Tm	Crystalline phase melting temperature
V	Volume

1. Introduction

In 1937 Dr. Otto Bayer decided to investigate the addition products of diisocyanates as a means of producing fiber materials with properties equal or superior to those of nylon, and which would not be covered under any DuPont patents. The polymer produced by Bayer was named polyurethane and has become one of the most flexible polymers with a wide range of properties and applications.

Polyurethanes are used in a wide range of applications, mainly because its properties may be easily tailored to vastly different end results, ranging from a stiff, thermoset material to a soft expanded elastomer. The tailoring of properties is generally associated with changes in the soft and hard segments, and in some cases the chain extender. A chart of the main applications of polyurethanes is shown in figure 1.1. and the market share of polyurethanes consumption is shown on figure 1.2.

Polyurethanes elastomers (PUEs) have excellent mechanical properties such as high abrasion resistance, toughness and high tensile strength. PUEs are often used in the automotive, carpeting and shoe industries, due to their properties [1]. The elastic recovery displayed by PUEs can be attributed to primary chemical crosslinks, but in many cases a different mechanism is approached, the aggregate of hard segments serves as anchors for the long flexible soft segment, responsible for the large elongations without yielding. However, their high temperature performance and chemical resistance are not adequate for many applications, and their low temperature elasticity is severely limited by the relatively high Tg of the soft segments making conventional PUEs unsuitable for very low temperatures [2]. Mainly due to the possibility of the tailoring of the properties of these polymers, polyurethanes compose a very significant market, with a yearly consumption estimated to reach seven billion pounds per year in 2005.

Fluorinating polymers has become a very attractive alternative for improving the thermal and surface properties of traditional polymers. The surface properties such as the contact angle generally increases, wettability and surface tension are reduced and thermal stability increases. [3]

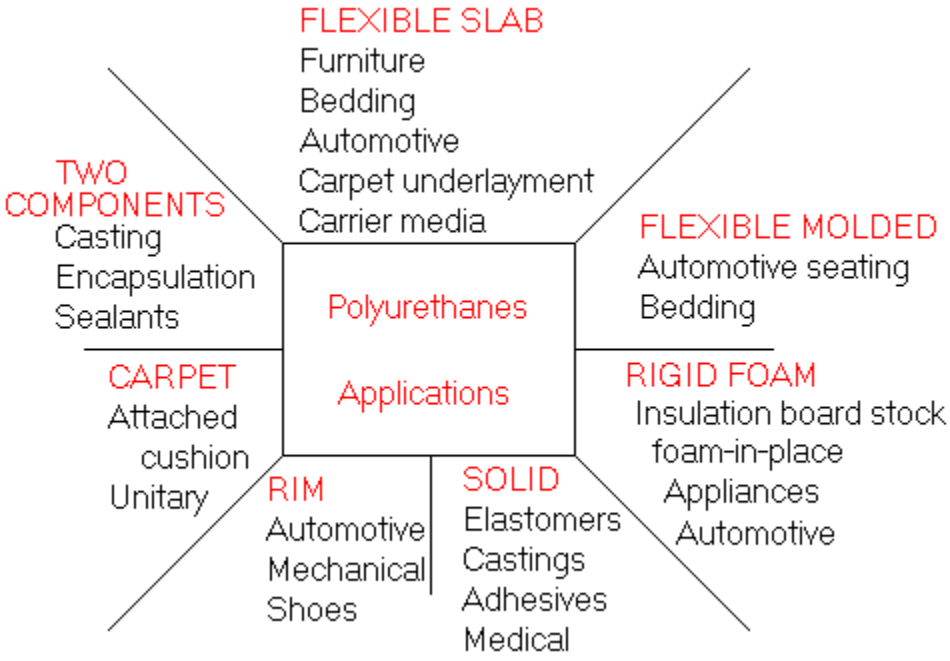


Figure 1.1. Main industrial applications for polyurethanes

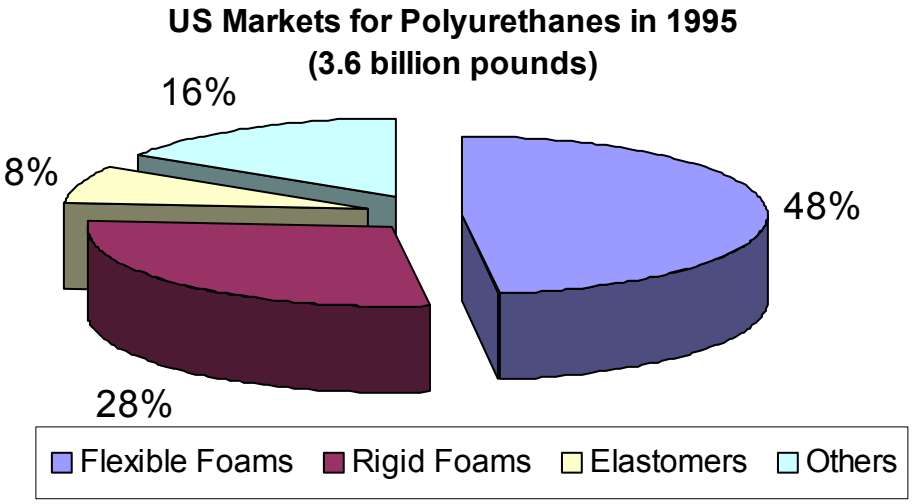


Figure 1.2. Market share of the polyurethane consumption in the US, 1995.

In some cases, the fluorinated segments may be concentrated on the surface of the material, generating a polymer that contains properties of the non fluorinated segment in its bulk and properties close to those of the fluorinated segment on the surface [4]. Polyurethanes with high molecular weights fluorinated segment exhibit surface properties characteristic of fluorinated polymers. [3]

For many applications, thermal-oxidation is a common problem in the aging of polymers and plastics. Once a polymeric product suffers extensive oxidation, the surface quality of the parts looses the original properties. In some cases, where the appearance is a key factor for the product's life span, as in most surface coating applications, yellowing, surface cracking and even changes in surface energies are very undesirable. Yellowing is the main concern of 4,4'-diphenyl methane diisocyanate (MDI) based polyurethanes [5].

The mechanism of the thermal degradation of any polymer and its by-producs should be comprehended prior to their commercial usage. This would allow engineers to use polymers that will maintain their properties for the proposed life span, and assure that during aging they generate by-products that do not compromise the initial purpose. The mechanical properties and degradability of PUEs based on MDI and polyethers have been studied but the influence of the incorporation of fluorinated structures on these materials is still unknown.

The prediction of fluorinated polyurethanes lifespan requires the understanding of the thermal-oxidative degradation process. The goal of the present work is to study the effect of fluorination on the thermal stability of elastomeric polyurethanes, based on polytetramethylene glycol (PTMG) and polypropyene glycol (PPG) soft segments with molecular weights of 2000. The fluorination was achieved by the use of a perfluoro polyether diol (Fomblin® Z-Dol 2000), the hard segment used was a 4,4'-diphenyl methane diisocyanate (MDI) and the chain extender (two step polymerization) was ethylene diamine (EDA). For achieving this goal, fluorinated samples with varying percentage soft segment perfluoro polyether diol substitutes were exposed for periods up to eight weeks at 120^{o}C and the changes in the materials were followed by dynamic mechanical analysis, thermal gravimetric analysis, Fourier transform infrared

spectroscopy. The exposure temperature (120^{o}C) was chosen because it accelerates oxidative processes and aging of the samples, yet it is below major degradation onsets of polyurethanes.

1.1. Polyurethanes Chemistry

Polyurethanes compose a class of materials that include all polymers with the urethane linkage in the main chain. The urethane linkage (figure 1.1.1.) is normally derived from the reaction of a diisocyanate with a diol. Polyurethanes are segmented copolymers composed of hard (diisocyanate) and soft (diol) segments. The synthesis of polyurethanes can be done through many different ways. The two step method involves the reaction of stoichiometrically designed solutions having two moles of diisocyanates for each mole of macro-glycol to form the so called "pre-polymers". The "pre-polymers" are then coupled through a second reaction with a chain extender resulting in a high molecular weight polyurethane chain. The choice of chain extender is of extreme importance, since some may form inter-chain hydrogen bonding - a function of the bonding angle between the chain extender and the pre-polymer, making on this case, difficult to thermally process the final product. The most commonly used chain extenders are ethylene diamine (EDA) and 1,4 butane diol (BTD), where the former generates a more thermally stable polymer and the latter generates a thermally processible polymer. The polyurethanes that contain the EDA on their backbone are called polyurethane-ureas, due to the urea linkage present on the main chain. BTD is another common chain extender used in PUs, with the advantage of producing thermally processible (and recyclable) materials.

The chemical reaction illustrated in figure 1.1.2. shows the origin of the urethane linkage. R and R' are derived from the reaction of diisocyanate and diol. The urea

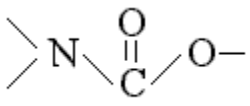


Figure 1.1.1. The urethane linkage.

linkage (figure 1.1.3.) is formed between the EDA chain extender and the isocyanate. Typical hard segments (diisocyanates) used on polyurethanes include 4,4'-diphenyl methane diisocyanate (MDI) or toluene 2,4-diisocyanate (TDI), while soft segments can be a wide range of chemicals, such as polyethers, polyesters and polycarbonates. Two very significant polyether soft segments used in polyurethanes synthesis are polyoxypropylene glycol (PPG) and polytetramethylene glycol (PTMG). The molecular weight of the soft segment plays an important role on the properties of the final polymer. It is common for polyurethanes based on PTMG to have crystalline regions if the PTMG molecular weight is greater than 1700. The lower molecular weight soft segments form stiffer polymers with lower tendency to phase segregation due to chain mobility restrictions.

A determining factor in the polyurethanes ability to be melt processible is the amount and nature of the hydrogen bonding. In figure 1.1.4., 'H' and 'S' denote hard and soft segments, respectively, and 'a' and 'd' are proton acceptor (carbonyl) and donor (NH). 1,4 butane diol (BTD) is a common chain extender for thermoplastic polyurethanes because the final morphology of the polymer does not involve too many hydrogen bonds. Polyurethanes with ethylene diamine (EDA) as chain extenders, for

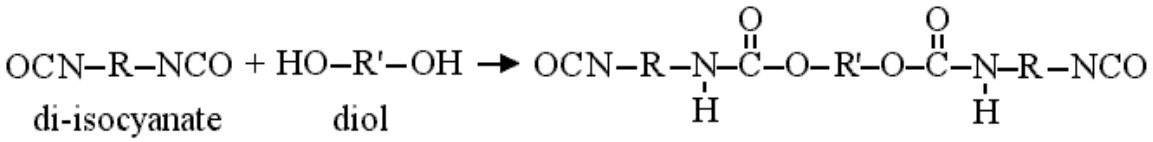


Figure 1.1.2. Step one of polyurethanes two step polymerization.

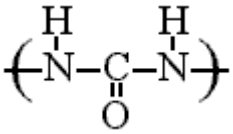


Figure 1.1.3. The urea linkage.

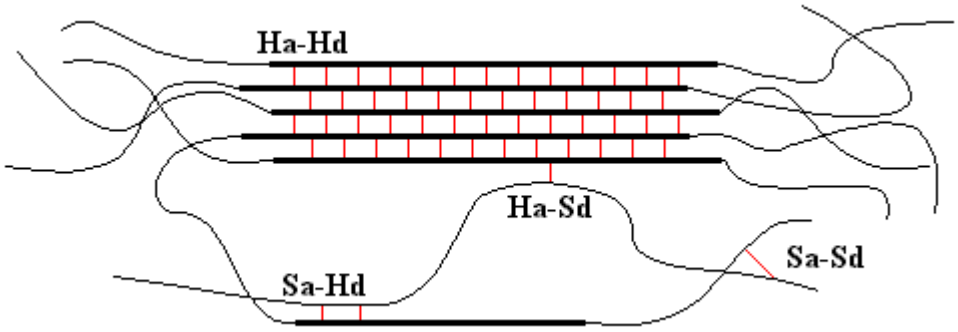


Figure 1.1.4. The four types of hydrogen bonds expected for segmented polyurethanes.

example, will produce a material that will not be melt processible due to the high proportion of hydrogen bonds. Increasing number of intermolecular bonding will increase the resistance to certain solvents, as well as the mechanical strength, wear and abrasion resistance, fatigue and overall durability of the material.

Polyurethanes are segmented copolymers. High molecular weight copolymers with chemically similar segments are assumed to be miscible or to have the tendency to present good mixing of the segments. Copolymer with miscible segments will have one transition temperature and one melting temperature. High molecular weight copolymers with significantly different segments are generally not miscible, or in other words, the copolymer segments will have the tendency to segregate the segments and generate a phase-separated structure. The phase separation occurs primarily due to incompatibility between the two segments and it is strongly dependent on several factors, such as the type, molecular weight, molecular weight distribution and the chemical compositions of the soft and hard segments and the chain extender. [6,7,8,9,10] In addition, the degree of phase separation will depend on the processing history of the material, casting, molding or annealing history. A phase separated copolymer will show characteristic behavior of both phases, or in other words, each individual segment will have their own Tm and Tg.

The degree of phase separation in copolymers may drastically affect the properties of the material, in terms of both chemical and mechanical behaviors. Phase separation in block copolymer can be desirable for a wide range of applications, such as biomaterials,

degradable films, elastomers and foams. Generally for elastomeric polyurethanes, the hard segment form domains that serve as physical anchors during deformation of the long soft segment. Similarly, for other applications, one component may be either soluble or degradable in target environments, allowing a vast number of engineering applications for these materials.

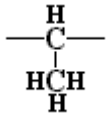
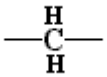
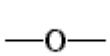
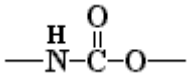
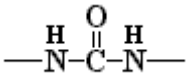
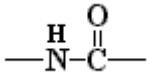
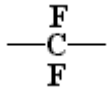
The molecular weight of each of the polyurethane segments affects the overall properties of the material. In the case of a short soft segment chain, the hard segments will have dominating effect on the polymer's properties while in the case of longer soft segment chains, elasticity may be enhanced. For soft segments that crystallize, higher molecular weights may increase the degree of crystallinity and therefore induce changes in the mechanics of the system.

The solubility parameters of the polyurethanes segments can be estimated by the cohesive energy and group contribution method [11]. According to the cohesive energy and group contribution method, each individual group contributes to the final solubility parameter of the segment, as seen on table 1.1.1. The values of E_{coh} and V, equation 1.1.1. may be used to determine the solubility parameter δ.

$$\delta = \left(\frac{E_{coh}}{V} \right)^{1/2} \qquad \text{Equation 1.1.1.}$$

Each of the segments of the polyurethane have a solubility parameter that varies according to their molecular weight and chain volume per mol. To find an overall value for chain volume and cohesive energy, the contributions of the groups are then added to the overall structure of the segment, according to its molecular weight.

Table 1.1.1. Cohesive energy influence of certain structures and their volume. [6]

Structure	E_{coh} (J/mol)	V (cm^3/mol)
	8140	34.5
	4940	16.1
	3350	3.8
	31940	71.4
	26370	18.5
	41860	14
	33490	9.5
	4270	23

1.2. Fluorination of Polyurethanes

While in most fluorinated polymers there are substitute fluorine atoms in the monomer, the fluorination of polyurethanes may be done by the incorporation of perfluorinated soft segments (generally having molecular weights between 1000 and 2000) during the polymerization. In the two-step polymerization for instance, the inclusion of the fluorinated soft segment is done on the first step, or in other words, during the formation of the pre-polymer. Low molecular weight fluorinated polyethers became available in 1996. Thus, only a few fluorinated polyurethane are commercially available. [2,12,13]

When perfluorinated segment is the only component of the soft segment, the final polymer will be considered to be 100 per cent fluorinated. In case other glycols are included in the synthesis of the polyurethane, then the stoichiometric proportion of the fluorinated and non-fluorinated segments will determine the percent fluorination of the final polyurethane. For instance, if there is a methylene diamine isocyanate – polypropylene glycol – ethylene diamine (MDI-PPG-EDA) polyurethane that is 50% fluorinated with a perfluoro glycol, the final stoichiometry will be 4 MDI : 1 PPG : 1 perfluoro glycol : 2 EDA.

In many cases, the perfluorinated portion of the polyurethanes have similar solubility parameter to the non-fluorinated soft segment. This similarity is of striking importance in terms of miscibility and the overall morphology of the polymer. During the second of the two-step polymerization, when the pre-polymers are joined in solution to form the complete polyurethane chain, good miscibility between the two fluorinated and non-fluorinated segments will allow good randomness of the chain structure (-non fluorinated-fluorinated-non fluorinated-fluorinated-), unlikely to happen if the two have different solubility parameters. The miscibility will also generate more homogeneously distributed fluorinated segments throughout cast films and through any processing technique.

The properties of fluorinated polyurethanes depend on composition. Generally, incorporation of fluorinated segments into polyurethanes leads to higher heat resistance,

better low temperature performance due to the very low glass transition temperature of the perfluorinated soft segment and the reduction in surface tension (more hydrophobic) and coefficient of friction, becoming invaluable for applications such as in coatings and seals. In addition, fluorinated polyurethanes generally become more resistant to hydrolysis. [2]

Figure 1.2.1. illustrates a general scheme for the complete chain of a 50% fluorinated PPG based polyurethane-urea (it is in reality random), where 'n' is the number of times PPG is repeated, and 'm' is the number of times the non-fluorinated polyurethane of equivalent molecular weight to the one shown here repeats itself. Figure 1.2.2. shows the influence of fluorinated segments on the thermal properties of PTMG based polyurethanes. [11] It is clear that the melting energy for the PTMG based polyurethane is reduced with the increasing degrees of fluorination, evidence that the crystalline regions are composed of PTMG segments.

Figure 1.2.3. shows the effect of fluorination on PTMG based polyurethanes. Note that the main difference in the absorptions is the significant increase of the 1222cm^{-1} band, attributed in part to the C-F stretching (combination absorption band).

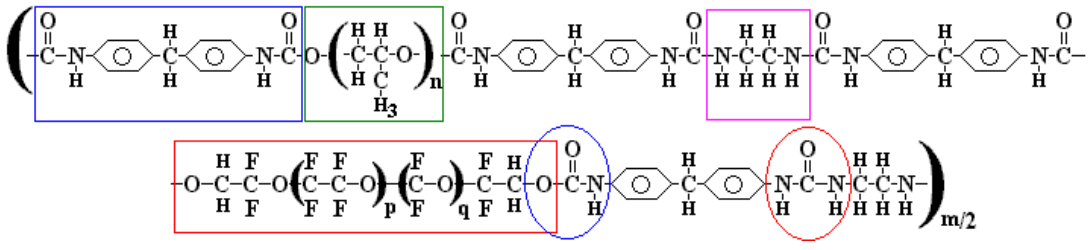


Figure 1.2.1. General chemical structure of a 50% perfluorinated MDI-PPG-EDA polyurethane-urea. The perfluoro segment illustrated is the Fomblin Z-DOL 2000® from Ausimont. Squares: blue- MDI, green- PPG, red- Fomblin Z-DOL 2000®, magenta- EDA. Circles: blue-urethane, red- urea.

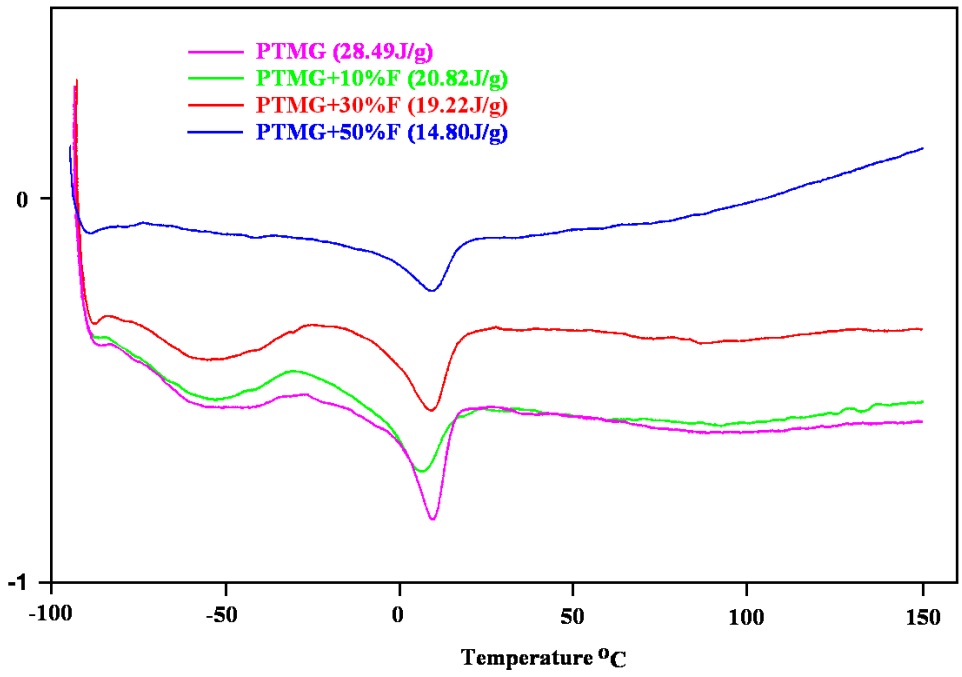


Figure 1.2.2. DSC results on the influence of fluorinated segments on PTMG based polymers. [11]

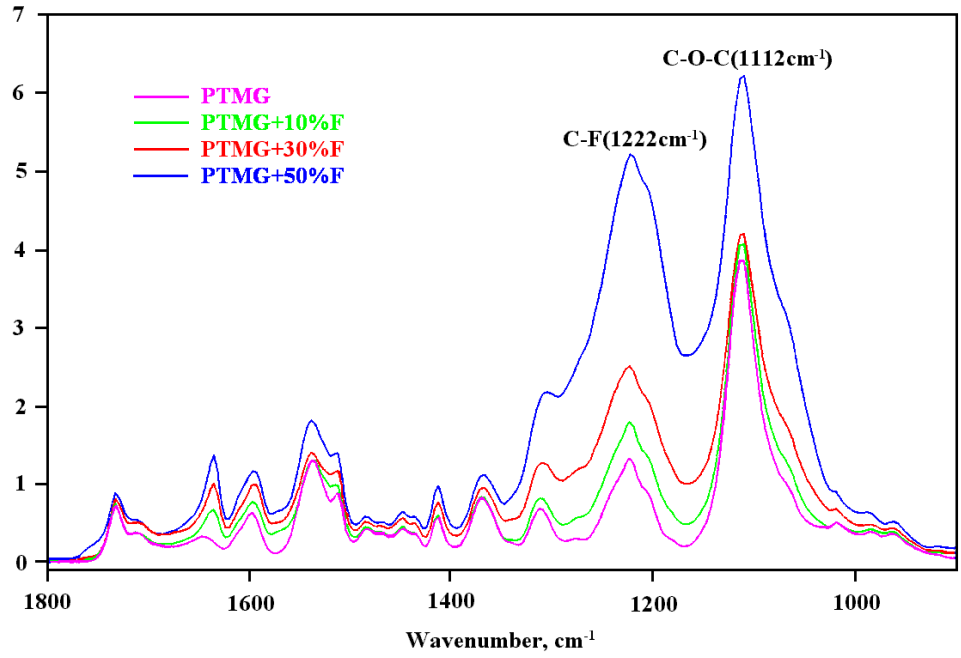


Figure 1.2.3. Infrared spectra of fluorinated segments on PTMG based polymers. [11]

1.3. Degradation of Polyurethanes

The use of polymeric materials in increasingly demanding applications has led in recent years to an upsurge in the study of polymer durability both in industrial laboratories and in universities and research institutes. Stabilizers are often added to polymers to extend their durability. Stabilizers act by a wide range of technological inhibition processes, specific terms have been coined to describe particular kinds of inhibition when the precise cause is known. Some examples of stabilizers used on the market are 'flame retardants', 'UV stabilizers' and 'antioxidants'. A combination of different stabilizers are normally called 'antidegradant' and they are used for the inhibition of different types of degradation mechanisms. The effectiveness of antioxidant (a common stabilizer for outdoor end-use plastics) is illustrated on figure 1.3.1. where the appearance of carbonyl groups can be seen in the 1700cm^{-1} region for the polymers without the stabilizer and with a thermal history.

The changes in physical properties of polymers during aging and its reasons cannot be separated. If further major advances are to be made in the improvement of the durability of polymers in service, a better scientific understanding will be necessary of the chemical and physical phenomena involved in polymer degradation. The ultimate criteria of the durability of a polymer component is the length of time it continues to perform satisfactorily under service conditions. The design of polymeric materials is therefore just as important as dimensional design and both are frequently interrelated.

In some applications as in agricultural mulching, the service life can be measured directly. In other applications intended for longer lifetimes, a real time test would not be economical. For instance, a PVC window would have to be exposed for over 30 years in a the environment for quality assurance, would be economically inadequate. Long term applications products require 'accelerated aging' tests which are intended to accelerate the effects of the environment elements that harm the polymer under service conditions. The interpretation of accelerated tests and their correlation with service tests lies at the center of the problem of selecting polymers for long term applications. In the design of a

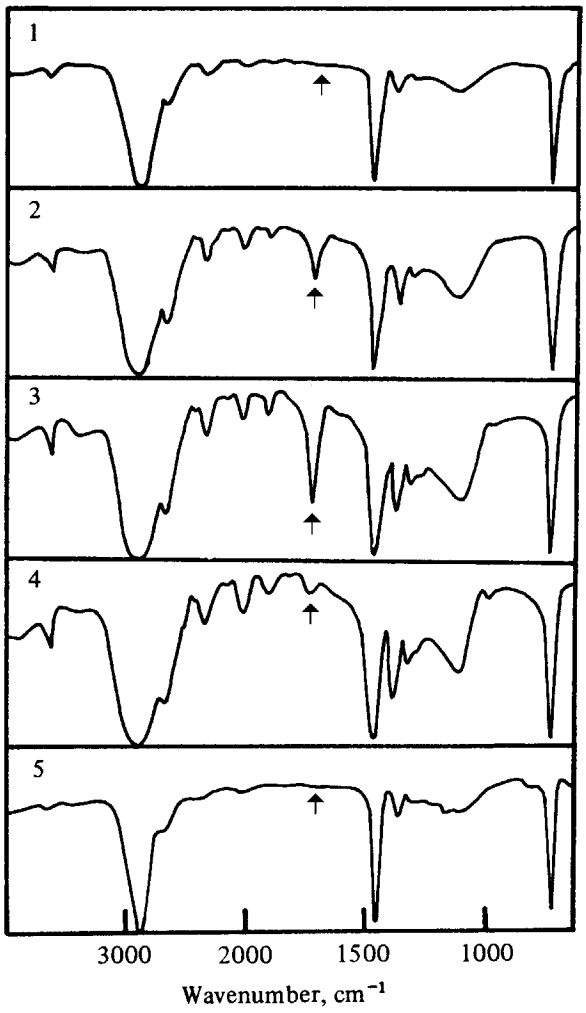


Figure 1.3.1. Infrared spectra of HDPE films with different histories: 1 with antioxidant after standing at ambient temperature for one year; 2 as 1 without antioxidant; 3 as 2 after standing for three years; 4 as 3 after treatment with an aerated medium inoculated with cultivated soil; 5 HDPE powder without antioxidant exposed to aerobic biodegradation for two years before molding to film with exclusion of air. [14]

polymer part, the physical and chemical phenomena involved in the process of degradation have to be understood and considered on its design.

A commonly used accelerated test for thermal oxidative stability is the 'air oven test'. This involves subjecting a suitably fabricated polymer sample (generally a film or a molded strip) to temperatures ranging from 70 to 150^{o}C. Mechanical properties of these films are then measured periodically until the properties are not adequate for the intended application of the polymer. The technological criteria used in the assessment of the deterioration of some polymers are less concerned with mechanical behavior than with change in appearance. Many polymers discolor during aging due to the formation of polyconjugated saturation. These phenomena can be followed by spectroscopic analysis.

Although all polymers degrade at high temperature without the presence of air, degradation is almost always faster in the presence of oxygen. Oxidation of hydrocarbons is normally auto-accelerating, i.e. the rate is slow or even negligible at first but gradually accelerates, often to constant values. Oxidative degradation is studied extensively due to its commercial importance. The initial effect of oxidative degradation is often quite subtle and difficult to detect. Chemical changes occur at random sites in an infinitesimal number of molecules in the mass. However these initial reactions are in random and small sites of the polymer, they initiate further oxidation during normal service life until obvious changes are evident. For this reason it is important to recognize all stages of degradation in the polymer's life cycle. Figure 1.3.2. illustrates the oxygen absorption during high temperature exposure of a certain polymer and the expected influence of additives on its composition.

Ground state oxygen is more common in the triplet state, i.e. it is a radical as illustrated by figure 1.3.3.(I). Although excited singlet oxygen as the one represented on figure 1.3.3.(II) can be important as an autoxidation initiator under certain circumstances, oxygen normally reacts with organic compounds in a radical chain reaction involving ground states. Each cyclical sequence of reactions (figures 1.3.4. III and IV) absorbs one molecule of oxygen and leads to the formation of a hydroperoxide. Since reaction III is a radical pairing process it has a low activation energy and occurs with high frequency. The second step (IV) on the other hand involves the breaking of a carbon-hydrogen bond

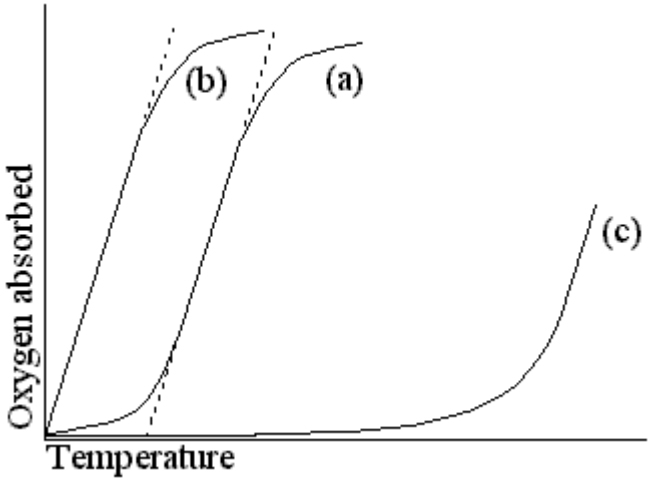


Figure 1.3.2. Idealized Oxygen absorption curves for oxidizing polymers: (a) pure polymer; (b) polymer with added hydroperoxide; (c) polymer with added oxidant.

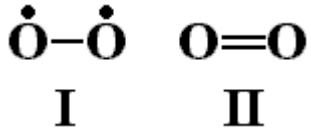


Figure 1.3.3. Forms of O_2 molecules of air.

Figure 1.3.4. General oxidation reactions of polymers.

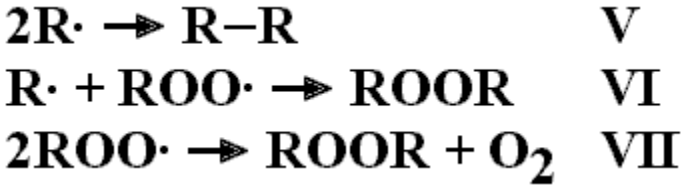


Figure 1.3.5. General termination processes for polymers.

and has a higher activation energy. In most polymers at normal oxygen pressure, the rate of step IV determines the overall oxidation rate.

The structure of the auto-oxidizing hydrocarbon and the oxygen concentration determine which of the termination steps illustrated on figures 1.3.5. V, VI and VII lead to the removal of radicals from an auto-oxidizing substrate. Since normally the reaction shown in figure 1.3.5.IV is rate determining, alkylperoxyl radicals are the dominant radical species present in auto-oxidation and termination occurs primarily through the reaction shown on figure 1.3.5.VII.

If oxygen access is limited by diffusion, for example during processing of polymers, the reactions shown on figure 1.3.5.V and VI may play an important role. Polyurethanes are a special case in terms of oxidation. The first polyurethanes to be developed were based on simple glycols where a high frequency of the carbonyl constituent was evident along the polymer chain, as shown on figure 1.3.6. The development of the polyether-urethanes, in which the simple glycol was replaced by a polypropylene glycol (figure 1.3.7.), resulted in a much greater oxygen sensitivity both during the manufacture of the polymer and during service. The oxygen attached to carbon activates the α-oxygen atom to hydroperoxidation. The well known tendency of diethyl ether to peroxidize in laboratory experiments illustrates the importance of this process. In this respect, the α-oxygen atom is about 20 times more effective than a methyl groups. [14] Consequently, polyether-based polyurethanes undergo the technological phenomenon of 'scorch' during manufacturing due to oxidative sensitivity of the polyether segment and occasionally blocks of polyurethane foam have been known to undergo spontaneous ignition shortly after manufacture due to peroxidation phenomenon.

The processing of PUs normally involves temperatures above the melting point, which enhances oxygen accessibility and triggers oxidation, especially for high residency times. Once the polymer is molded into a final shape, the thermal oxidation process will continue slowly, throughout the service life. Most of the oxidation of a polymer occurs

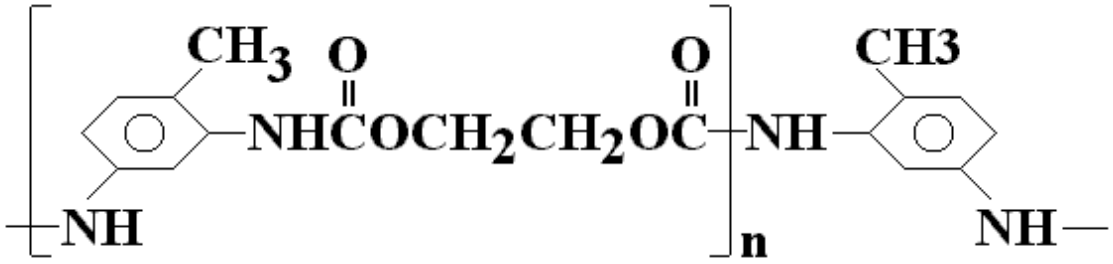


Figure 1.3.6. The structure of the first polyurethane.

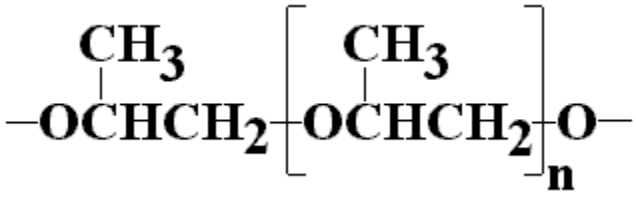


Figure 1.3.7. Structure of PPG.

during long-term aging, and a different type of stabilizer is required to protect the material under these conditions.

Thermal degradation of PUs based on methylene diisocyanate (MDI) is believed to begin on the hard segment, whereas weight loss is related to the degradation of the soft segment. [5] The degradation of the hard segment is associated with the yellowing of the polymers, caused by the generation of conjugated double bonds, which limits the application of these polymers to areas where appearance is not important. There are two modes of thermal decomposition that have been proposed for urethane linkages: (1) depolymerization back to alcohol and isocyanate and (2) cleavage of the C-O bond of the urethane through a cyclic mechanism that generates amine, olefin and CO_2. [16]

Urethane may dissociate into the isocyanate and polyol (figure 1.3.8.). This reaction is reversible as long as the isocyanate is not lost to a side reaction. The second reaction produces a primary amine and olefin. The third reaction produces a secondary amine. Since the latter reactions generate CO_2, they are irreversible. The thermal dissociation is, of course, directly associated with the temperatures the polymers are

submitted to and the exposure time. Some important onset temperatures are described on table 1.3.2.

In polyether-urethanes, the ether is the weak link with respect to thermal oxidation. The thermal oxidation proceeds via a free radical mechanism. Heat causes a hydrogen extraction at an α-carbon to the ether linkage. This radical is subject to oxygen addition and forms a peroxide radical. The peroxide radical then extracts another hydrogen from the backbone to form a hydroperoxide. The hydroperoxide radical then decomposes to form an oxide radical and the hydroxyl free radical. The order of thermal oxidative stability is: Ester > urea > urethane >> ether, as illustrated on figure 1.3.9.

The oxide radical will cleave at either of two places (figure 1.3.9.). One, it may cleave at the carbon bond adjacent to the oxide radical. If so, a formate is formed. Two, if the cleavage is at the carbon-oxygen bond, aldehydes are formed. The order of stability of polyethers to thermal oxidation: PTMG is more stable than polyethylene oxyde glycols (PEOG), which are more stable than PPG.

Although the basic mechanisms of PUs degradation and bonds that are prone to cleavage are known, thermal stability for these polymers is governed not necessarily by the weakest link in the chain but often by the most frequently occurring one and by the environment of the given groups. [3] It was shown that the polyether soft segment and the MDI/piperazine hard segment are more stable when mixed in the copolymer than in separate phases. [3] To explain such behavior, Fergunson [3] studied the degradation of each segment separately. It was found that poly(tetramethylene oxide) (PTMO) degrades easily in air by oxidation at the β-carbon next to ether. Breakage of the C-O bond and subsequent unzipping was proposed as the mechanism in an inert atmosphere. [4, 17]

Table 1.3.1. Common mechanisms of polyurethanes depolymerization. [16]

Depolymerization reactions of polyurethanes		
Hydrolysis	Thermolysis	Oxidation
Photolysis	Microbial	Biologically induced stress cracking
Solvolysis	Pyrolysis	

Table 1.3.2. Important onset temperatures for polyurethanes.

Linkage	Dissociation onset (^{o}C)
Aliphatic allophanate	85-105
Aromatic allophanate	100-120
Aliphatic biuret	100-110
Aromatic biuret	115-125
Aliphatic urea	140-180
Aromatic urea	160-200
Aliphatic urethane	160-180
Aromatic urethane	180-200
Di-substituted urea	235-250

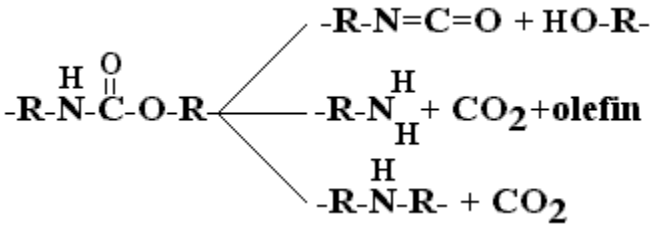


Figure 1.3.8. Thermal degradation mechanisms of urethane linkages.

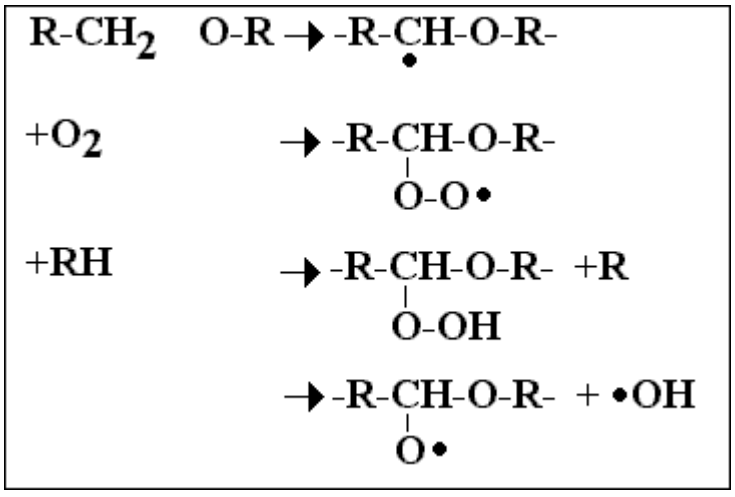


Figure 1.3.9. General thermal oxidation mechanism of polyester-urethanes. [16]

Transurethanization, a process analogous to transesterification in polyesters, was suggested to enhance the vulnerability of the polyether soft segments in polyurethanes, once the amines from the hard segment may act as traps for radicals formed in the soft segment. The thermal stability of more complex systems, such as segmented polyurethanes, depends both on segment lengths and their concentration. [4, 17]

1.4. Contact Angle as a Function of Surface Wettability

The contact angle between a droplet of a solvent in a solid's surface may be used as an indirect way to study the surface properties of the solid, such as surface tension and consequently the susceptibility of the material to spread the solvent in the surface (wettability). The inside angle formed by the droplet on the surface is called contact angle and was first studied by Young [18]

In the case of hydrophobic surfaces, the physical significance of the contact angle is quite clear. For example, to develop water repellency, it is desirable that the contact angle is as large as possible, as in the case of water repellant coatings and fabrics. On the other hand, if a water absorbing surface is desired, then the contact angle is desired to be as small as possible, as in the case of absorbing and reactive materials. [19]

The study of the contact angle has a special significance in terms of surface modifications treatments or degradation. Surface treatments may enable the use of certain materials due to properties enhancement and these properties should be maintained with the projected lifetime of the product. With the changes in the surface properties, such as in groups attachment (in some surface treatments) or in the chain breakdown, the surface properties may induce significant changes in the wettability. While in the field, these treatments may suffer changes and the critical properties could drop to below acceptable levels, making the study of these properties very relevant, especially for coating materials.

The surface features that might be of interest are elemental composition (and its gradients), chemical bonding (molecular composition), structures and geometry (topography). Many of the current experiments used to determine surface properties are

indirect tests, and the most significant are contact angle measurement, ellipsometry, infrared absorption and attenuated total reflection spectroscopy (ATR). Ellipsometry measures the intensities and polarization of light reflected on surfaces and contact angle measures the angle of a solvent droplet on the sample's surface, as illustrated on figure 1.4.1. The angle θ is a direct function of the wettability of the solid surface in relation to the solvent used. The value for θ is extremely important for certain applications, when the surface interaction of certain liquids become important (car waxes, printer ink, paints, glues, etc). Surface tension may also be determined from the contact angle according to equation 1.4.1.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\theta \qquad \text{Equation 1.4.1.}$$

where γ_{SV}, γ_{SL} and γ_{LV} are the surface tension of the solid/vapor, solid/liquid and liquid vapor, respectively.

A common way to increase the contact angle and therefore reduce the wettability of the surface of the polymer, is by including fluorinated groups to the backbone. Fluorinated segments generally are very polar in nature due to the intrinsic properties of fluorine, it normally makes the polymer more hydrophobic. For coatings, such as in cooking pans, boat hulls and roof coatings, this gain in contact angle is very appreciable and fluorinating traditional polymers has been a common practice for these reasons. [20]

The incorporation of fluorinated groups in the polyurethane chemistry generally increases the contact angle measurements. [20, 21] The hydrophobic characteristic of the surface appears to plateau for higher concentrations of the fluorinated group in the polymer (around 7-10%wt). [21] Taking into consideration that in the case of

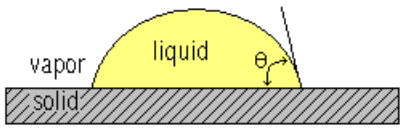


Figure 1.4.1. Contact angle measurement scheme.

polyurethanes, the soft segment (the macroglycol) is generally is substituted by a fluorinated segment such as Fomblin®, a perfluoro polyether diol, the enhanced polarity of the fluorinated segments and presence of tertiary nitrogen atoms increases the overall polarity of the polymer surface. [21]

Surface tension is generally determined through the assumption that plot of the cosθ versus the surface tension of different solvents of known surface tension gives a linear correlation (Zisman plot), as shown on figure 1.4.2. [22] This allows the extrapolation of the linearized curve to one, giving a critical surface tension, that implies a liquid should have at least this critical value of surface tension to be able to spread in the solid's surface. In fact the correlation is not strictly linear, but it gives a good idea of the critical value of surface tension, which is equal or smaller than the true surface tension of the solid.

The extent of wettability is correlated to the chemical groups and characteristics of atoms present on the surface of the solid. When water is used as the solvent (the most frequently used, actually), the hydrogen atoms have the natural tendency of becoming positively polarized. Due to its small size and mass, it readily interact with neighboring electronegative atoms such as nitrogen, oxygen and in special, fluorine, affecting the wettability of the solid. [23]

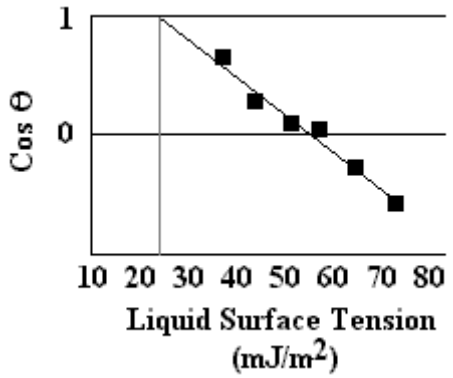
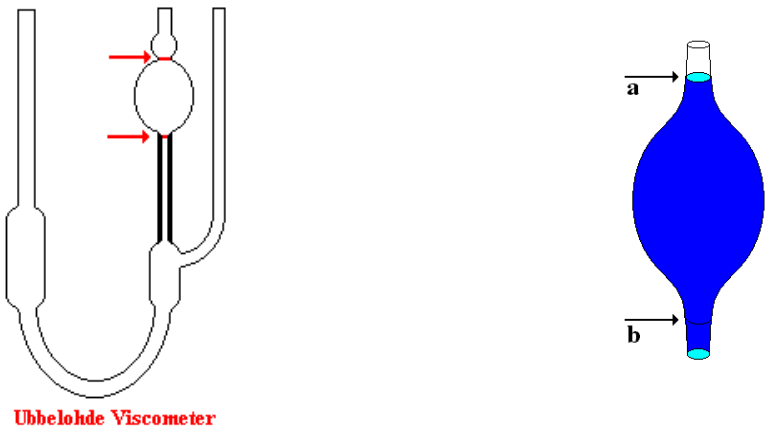


Figure 1.4.2. Illustration of a Zisman plot for a very hydrophobic solid. [22]

1.5. Intrinsic Viscosity

Soluble polymers are notorious for being good thickeners for applications such as shampoos and ice cream. This effect is caused by the fact that these polymers make solutions more viscous, in great part due to the higher molecular weight of these materials, that make the whole solution more difficult to flow due to the greater hydrodynamic volume of the molecule (the volume of the coiled polymer molecule takes in a solution). This is the main phenomena involved in intrinsic viscosity studies. The greater the thickening effect, the higher the molecular weight of the polymer. Also, the bigger the molecule is, the stronger the secondary forces are, once the solvent molecules will also be strongly bound to the polymer. This enhances the slowing down effect on the entire solution.

The polymer solution viscosity is a function of the time necessary for the solution to flow through the two marks (a and b), as illustrated on figure 1.5.1. That time will be then compared with the times for different solution concentrations. The time needed for the solution to flow through the two lines is called efflux time, 't'. On this case, "t_0" will be the time for the flow of the pure solvent and "t" the time for the solution at a known concentration. The ratio between the two flow times is called relative viscosity ($\eta=t/t_0$).



(a) (b)

Figure 1.5.1. (a)Viscometer scheme and (b) Detail of flow measuring area.

The specific viscosity and reduced viscosities can also be determined for all measures of different concentrations by the following equations:

$$\frac{t - t_0}{t_0} = \eta_{sp}$$ Equation 1.5.1.

$$\frac{\eta_{sp}}{C} = \eta_{red}$$ Equation 1.5.2.

where C is the solution concentration.

By plotting the viscosity versus the concentration, a plot similar to the one illustrated on figure 1.5.2. can be generated.

The slope of the plot is then called k'. The extrapolation of the curve, back to zero concentration, gives the intrinsic viscosity (y-intercept). As viscosity varies with concentration, the intrinsic viscosity is the value at a hypothetical "zero concentration". This gives an equation in slope intercept form, where ”m” is the slope of the line and b is the y-intercept.

$$y = mx + b$$ Equation 1.5.3.

$$\eta_{red} = k'[\eta]^2 C + [\eta]$$ Equation 1.5.4.

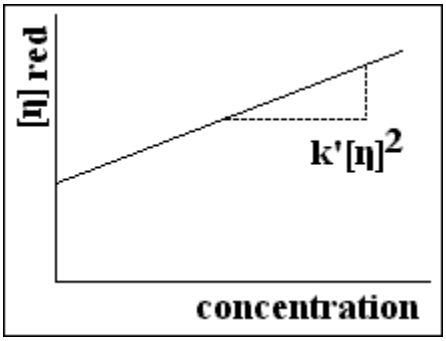


Figure 1.5.2. General plot of the reduced viscosity versus the solution concentration.

$k'[\eta]^2$ is the slope of the line and $[\eta]$ is the y-intercept. The intrinsic viscosity is an important number, once it's the one that will be directed correlated to the polymer's molecular weight.

A second way to calculate the intrinsic viscosity is by using the relative viscosity. The natural logarithm of the relative viscosity divided by the concentration of the solution gives the inherent viscosity. Now there's a different inherent viscosity for each concentration measured. A plot of inherent viscosity on the y-axis, and concentration on the x-axis will also give the intrinsic viscosity on the y-intercept, a way to check the data calculated for the reduced viscosity, as illustrated on figure 1.5.3.

The intrinsic viscosity is generally correlated to the molecular weight of the polymer by the use of the Mark-Houwink equation (equation 1.5.5.), where 'M' is the viscosity average molecular weight, K' and a are Mark-Houwink constants for the specific polymer and solvent used in the experiments.

$$[\eta] = K' M^{a}$$ Equation 1.5.5.

For most polymers, the Mark-Houwink constants are known and published, but for tailored polymers such as polyurethanes, the molecular weight may not be easily determined by following Mark-Houwink's equation. On such cases, the intrinsic viscosity may be used to qualitatively study the changes in MW by the changes in viscosity.

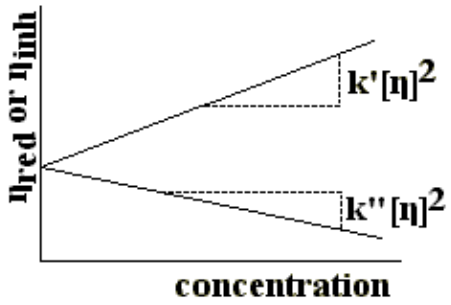


Figure 1.5.3. Reduced and inherent viscosities versus solution concentration.

1.6. Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) is a thermal analysis which examines the mass changes as a function of temperature in scanning (non isothermal) or as a function of time in the isothermal mode. Not all thermal events bring results about a change of mass, such as melting, glass transition, crosslinking or crystallization, but there are some exceptions which include vaporization, sublimation, absorption, oxidation, reduction and degradation. The main application in the field of polymers for TGA is in the study of degradation of polymers, to characterize the thermal stability of these materials under controlled conditions. Factors such as heating rate, sample mass, surface area and volume are important in terms of heat transfer, especially for materials with low heat conduction coefficient. TGA results are generally expressed in terms of mass versus temperature for the non isothermal testing and mass versus time for the isothermal testing. Figure 1.6.1. illustrates a typical non isothermal TGA test result of a single stage reaction, where the temperature interval between T1 and T2 is the reaction interval. [24] Interpretation of TGA data is often facilitated by comparison of other techniques. The gas produced on the reaction interval can be collected in more sophisticated thermal analyzers and it generally contains rich information that gives away the mechanism of the reaction.

A scheme for classifying TGA curves has been proposed [25, 26] where the curves are classified according to their shape into one of seven categories. Each category is schematically represented in figure 1.6.2. Curve ‘A’ in figure 1.6.2. shows a test in a temperature range where no significant mass changes occurred. Curve ‘B’ shows an initial mass loss, generally the result of low molecular weight particles associated with synthesis or sample preparation (residual solvent, for instance). Curve ‘C’ is a single stage decomposition reaction where the initial and final reaction temperatures are the limits for the reaction characterization.

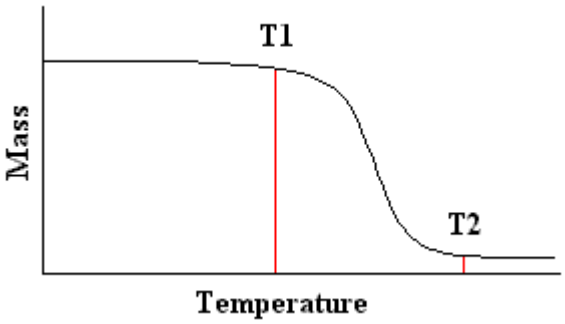
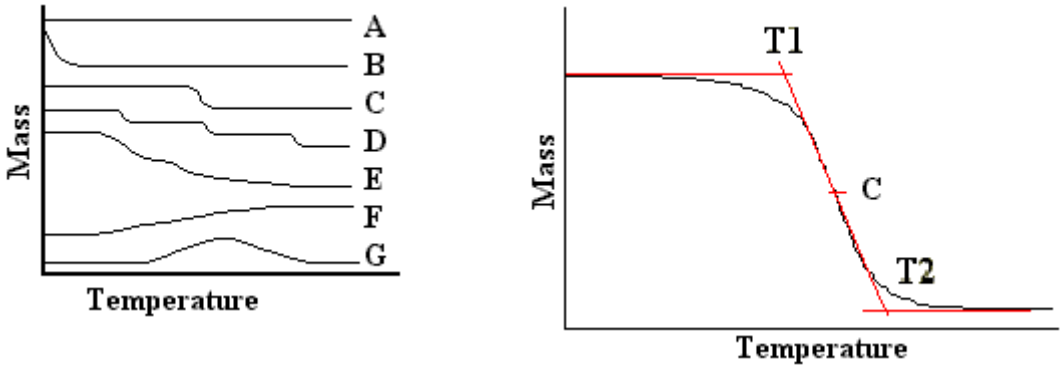


Figure 1.6.1. Typical TGA result for a single stage reaction.



(a) (b)

Figure 1.6.2. TGA curves. (a) Classification according to Duval [1.6.2.] and (b) defining T1, T2 and C.

Multi stage decomposition TGA are shown on curves ‘D’ and ‘E’. The main difference between ‘D’ and ‘E’ is the degree of phase separation in a multiphase polymer. On ‘D’ each phase can be well appointed, due to good difference in reaction temperatures, but the ‘E’ curve shows insufficient temperature separation between the onset of reactions between the phases. In the case of interacting atmospheres, curves ‘F’ or ‘G’ may be obtained. Surface oxidation generally is attributed to be the case for obtaining curves as ‘F’, and ‘G’ degradation would occur after surface oxidation.

For calculations and study of TGA curves, standards from ISO (International Standards Organization) are the most commonly used. The intersection of the extrapolation of the flat portion prior to the reaction onset and the extrapolation of the slope is defined as T1 (figure 1.6.2.b.). Analogously, the intersection of the extrapolation of the flat portion post reaction and the extrapolation of the slope define T2. ‘C’ is the median height and is characterized by being the maximum reaction point. In the case of multiple stages reactions, the first reaction will be the one that happens first.

1.7. Infrared Analysis

Infrared (IR) spectroscopy is an extremely useful technique to identify chemical compounds and quantify functional groups in molecules. Stretching, deformation and vibration of bonds in organic molecules give rise to specific absorptions of infrared radiation, the absorption being a function to the number of active groups. [27] The wavelength generally covered is from 5000 to mid-range 200 cm^{-1} (wavenumbers). Radiation absorption occurs at specific frequencies for particular bonds, so that a polymer with a variety of bonds has a multiplicity of absorptions, which represents a “fingerprint” for the material. In an infrared spectrum of absorbance versus wavelength, the absorption bands are compared and analyzed by the assignment to certain chemical groups and is a function of the chemical environment and nature of the chemical bonds. [28]

The absorption of IR radiation takes place when the vibrational energy of the chemical groups in the molecules is matched with the energy of incident IR radiation and there is dipole moment change during the excitation generated by the interaction of the

molecules with the electric field component of the electromagnetic radiation. Generally, the more dipole moment generated, the more intense the absorption in the spectrum.

The absorbance obtained from each functional group active for IR radiation can be expressed by the following equation:

$$A = K(M \cdot E) = K(ME)\cos\beta \qquad \text{Equation 1.7.1.}$$

where 'K' is a proportionality constant, 'A' is the absorbance, 'β' is the angle between the transition moment vector 'M' and 'E' is the electric field vector. As 'M' is determined by its magnitude and the molecular chain direction, the maximum absorbance will occur when 'β' is zero, i.e., the polarizing and the transition moment directions are parallel. If there is no preferable direction, the absorbance for those groups are equal. For this reason, this procedure is used for determining preferable molecular orientation in polymers. [28]

For comparing absorption bands for different test samples, where the intensities change according to the individual thickness of the samples as well as the population of chemical groups assigned to the wavenumber, rationing the peaks of interest to a reference peak, generally C-H stretching, is done. C-H stretching band (~2860cm^{-1}) is a good reference peak due to its good stability and frequency, assuming the samples in question have not been through treatment that affects this region. [16] A list of band assignments for polyurethane groups is shown on table 1.7.1. In the case of thermal exposure at temperatures below the urethane linkage onset, for instance, the urethane region a good reference as well. Depending on the type of study, the (C-O-C) absorption can be an excellent reference once it is a very strong absorption in polyurethanes spectra.

For hydrogen bonded PUs, the study of the variations of the urethane carbonyl and urea carbonyl hydrogen bonding is of great importance. The amount of hydrogen bonding on these polymers may drastically change their mechanical and thermal behaviors. PTMG based PUs for example, tend to hydrogen bond much more frequently than PPG based PUs due to the presence of the α-carbon on the PPG. Figure 1.7.1. shows the ideal case for hydrogen bonding of all possible cases for a PPG based polymer (MDI+PPG+EDA), with all carbonyl but one being hydrogen bonded to a neighboring

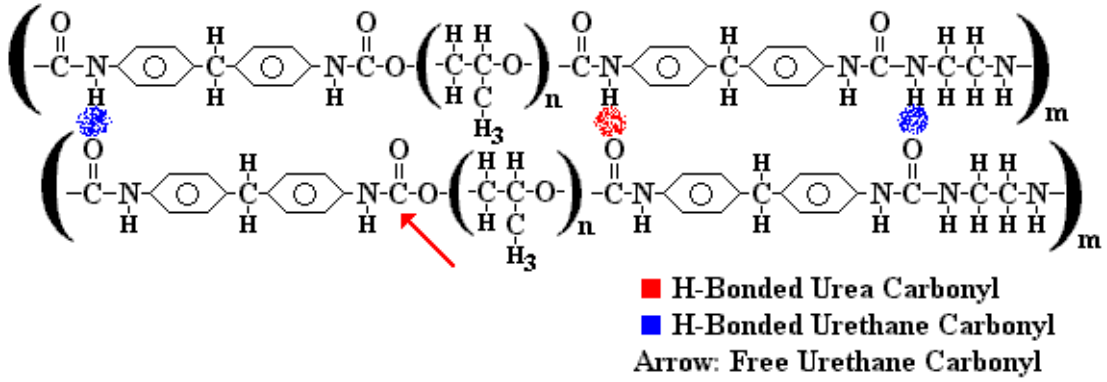


Figure 1.7.1. Structure of ideally ordered MDI+PPG+EDA polymer and its carbonyl groups.

Table 1.7.1. Assignments of wavenumbers for chemical groups in PTMG and PPG based polyurethanes.

Wavenumber (cm^{-1})	Assignment	Mode
3307-3287	(N-H) urea urethane, H-bonded	Stretching
2871-1856	(C-H) in CH_2	Asymmetric stretching
1732-1727	(C=O) free urethane	Stretching
1718-1709	(C=O) H-bonded urethane	Stretching
1649-1634	(C=O) H-bonded urea	Stretching
1599-1591	(C=C) aromatic ring	Stretching
1547-1532	(C-N)+(N-H) urethane	Stretching+bending/scissoring
1491-1459	(C-H) in CH_2	Asymmetric scissoring
1473-1446	(C-H) in CH_2	Symmetric scissoring
1412	(C=C) in aromatic ring	Stretching
1370	(C-H) in CH_2	Bending and Wagging
1310	(C-H) in aromatic ring	Scissoring
	(C-N)	Stretching
1270-1230	(=C-O-) ethers	
1221	(C-N)+(N-H)	Stretching+bending/scissoring
1225	(C-F)	
1200-1180	(O=CH-O-R) Formates	Stretching
1113-1105	(O=C-O-C) of urethane,	Symmetric stretching,
	(C-O-C) of ether	Stretching
965, 820	(C-H) aromatic ring	Bending or twisting
773	(O=C-O) of urethane	Bending or wagging

chain. In a real case, randomness and chain flexibility promotes less hydrogen bonding than presented on figure 1.7.1., and also the bulky atactic methyl group would lead to greater disorder in the system.

1.8. Dynamic Mechanical Analysis

A polymer under stress will deform as illustrated on figure 1.8.1., with a relaxation time required for straining according to the applied stress. If the stress is constant, the material will absorb some of this energy by deforming immediately and slowly relax to an equilibrium point. If the stress is applied with a certain frequency (periodic), then the recovery will also depend on a relaxation time. This analysis is of great importance especially for materials that creep easily.

For dynamic mechanical analysis, the sinusoidal strain ε can be expressed in terms of its angular frequency ω (2π times the frequency in Hz) and ε_0 (strain amplitude), if the material is considered to be elastic (obeys Hooke's law), as shown on equation 1.8.1.

$$\varepsilon = \varepsilon_0 sin\omega t \qquad \text{Equation 1.8.1.}$$

The stress response generated by polymer specimen is also sinusoidal but is read with a delay due to the viscoelastic properties, generally called phase lag or Tanδ. The stress is generally divided in two components, one in phase (E') and one out of phase (E"). The sum of the two components gives a complete equation for stress, as shown on equation1.8.2.

$$\sigma = \sigma_0 sin\omega t \cdot \cos\delta + \sigma_0 \cos\omega t \cdot sin\delta \qquad \text{Equation 1.8.2.}$$

By using the stress strain relationship ($\sigma_0 = E\varepsilon_0$), equation 1.8.1. becomes:

$$\sigma = \varepsilon_0 E' sin\omega t + \varepsilon_0 E'' \cos\omega t \qquad \text{Equation 1.8.3.}$$

where

$$E' = \frac{\sigma}{\varepsilon} \cdot \cos\delta \qquad \text{Equation 1.8.4.}$$

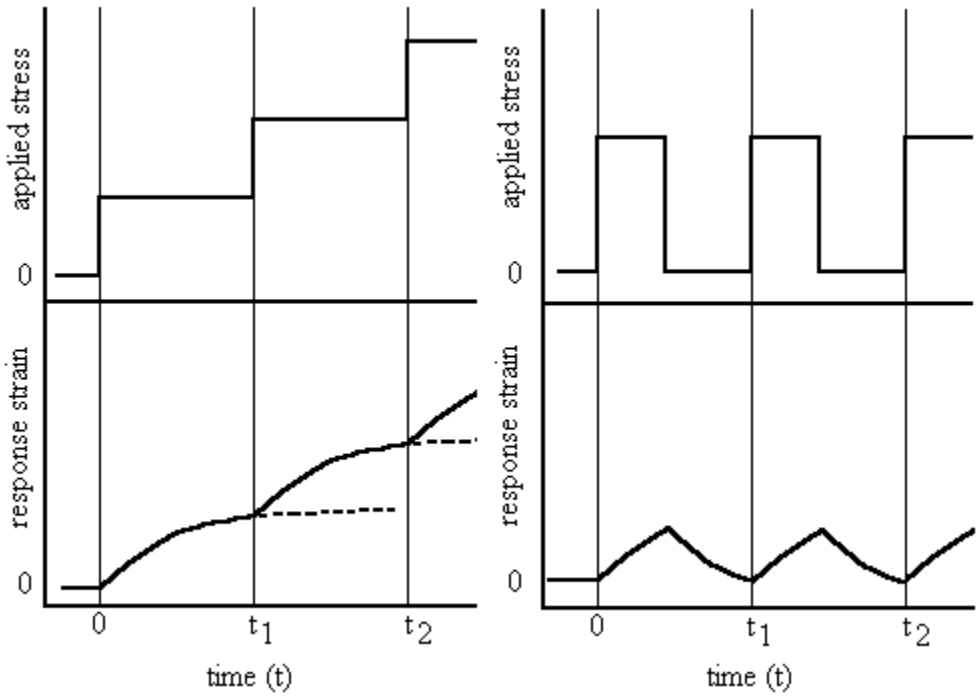


Figure 1.8.1. Applied stress and response strain for a viscoelastic material.

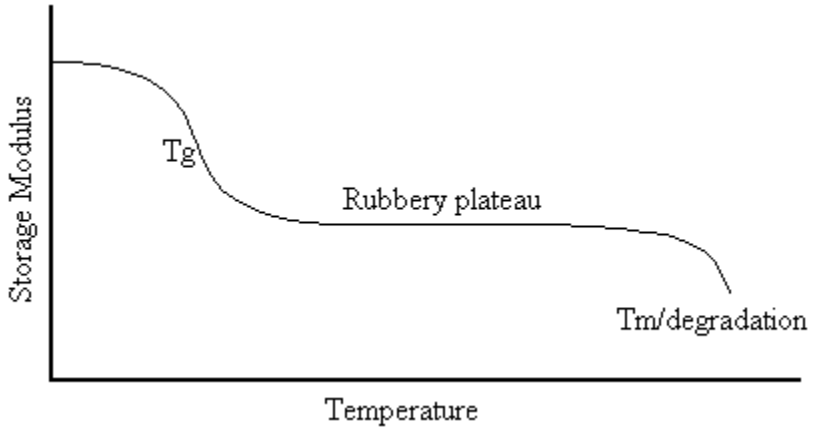


Figure 1.8.2. Typical behavior of homopolymer elastomers.

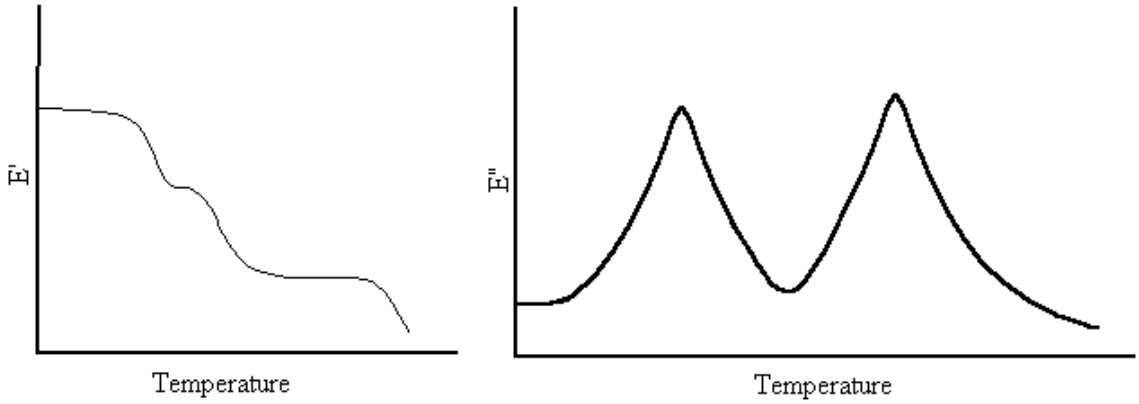


Figure 1.8.3. E' and E'' curves for highly segmented polymers.

and

$$E'' = \frac{\sigma}{\varepsilon} \cdot \sin\delta \qquad \text{Equation 1.8.5.}$$

Perhaps the most used form of DMA data representation is the ratio of the two components of the modulus, or the tangent (sin/cos) of δ, or Tanδ. The Tanδ curve will have a peak deflection for each transition, and is widely used for determining transitions. In some cases, the loss modulus is preferred due to its better defined transition temperature.

The transition temperature determined from the loss modulus differs from the one determined by the Tanδ. This implies that for consistency, in a series of experiments, all transitions must be determined by following the same method. In addition to the steepness of the transition temperatures regions in the storage modulus versus temperature curve yields qualitative information regarding the extent of phase separation in segmented block copolymers such as in polyurethanes. [36] For ideally mixed phases, a single peak would be observed. In the event of further phase mixing due to some process, different peaks may shift to temperatures intermediate to those of the individual phases. If the two phases have very different transition temperature and they are very segmented, then two transitions will occur, at temperatures lower than the rubbery plateau.

Since the extent of phase separation will significantly influence the mechanical behavior of copolymers (especially in the transitions region), molecular weight and properties of each component of the material will play important roles on the transition curves. Supposing the two segments are long enough to segregate, the compatibility of the two segments, will determine whether there will or will not happen segregation. If there is phase separation, the transitions will tend to happen closer to the transition temperature of each individual segment, and if there will not be phase separation, an intermediate temperature.

The compatibility may be correlated to an estimated solubility of each of the segments of the chain, using Dunkel approach. [6] Dunkel's method for estimating the solubility of liquids is still used currently for estimating polymer solutions miscibility. It takes into consideration each group that composes the polymer molecule, and the overall weight into a cohesive force, as illustrated on equation 1.8.6.

$$F = E_{coh} V (298))^{1/2} \qquad \text{Equation 1.8.6.}$$

In the case of polyurethanes, materials that are notorious for having physical crosslinks, a relatively long rubbery plateau region appears after the glassy state with a less sharp drop in modulus than ordinary amorphous homopolymers [16,31]. The length of the rubbery plateau is important for all polymers, since it defines the usable temperature region, especially for elastomers as polyurethanes.

The inclusion of fluorinated soft segments in polyurethanes elastomers chemistry is an alternative not only to enhance the low temperature properties of these polymers but also acquire some of the surface properties of the fluorinated segments. Typical fluorinated segments have very low glass transition temperatures (generally below –120^{o}C) and the Tg is a function of the O/C ratio, decreasing with increasing oxygen content [32,33]. In addition, the soft fluorinated and the hard segments are generally not compatible, leading phase segregation [34].

Kim [31] found that a reduction in breadth at half height of the tan δ and E" is attributed to an increase in micro-phase separation. The reduction was observed for higher molecular weight soft segments fluorinated polyurethanes, which suggest that

PTMG and PPG polymers phase separation is dependent on the molecular weight of the soft phases. Kim used soft segments with molecular weights varying from 1000 to 2000.

Figures 1.8.4. and 1.8.5. show the effect of degree of fluorination on PTMG and PPG based polymers. Note the Fomblin® transition temperature is around –140^{o}C, but due most likely to phase mixing (to PTMG and PPG) this temperature shifted to higher values. In addition to this, note that the intensity of the Tanδ changes with the degree of fluorination. As the curves in question represent E"/E', there is a mechanism involving either an increase in the loss modulus or a decrease in the storage modulus with the presence of the fluorinated segment.

In summary, general conclusions from other works primarily show that the soft segment transition directly depends on the extent of phase mixing which varies with hard segment; lower molecular weight soft segments lead to a higher Tg polymer because of higher amount of phase mixing, i.e., the chemical structure and composition are the most important factors to determine the degree of phase separation and will play an important role on the mechanical behavior of the resulting polymer.

In dynamic mechanical testing, the transition temperatures will also be a function of the frequency of the sinusoidal forces applied to the sample. That is due to the fact that a higher frequency implies in shorter periods of time for the polymer chain to conform to the strain. The relaxation delays as a function of the frequency in DMA tests can be used to calculate the activation energy of the transitions [35]. Activation energy results are widely used for the determination of domains influence in the properties of the polymers and the monitoring of changes in the chemical structure of materials.

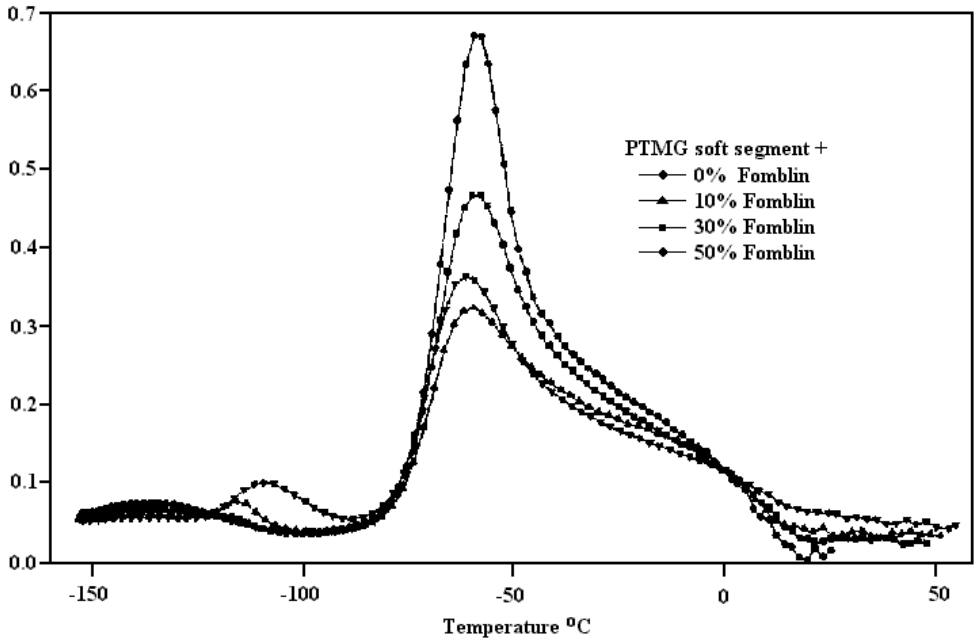


Figure 1.8.4. Fomblin® influence on a PTMG soft segment polyurethane. [11]

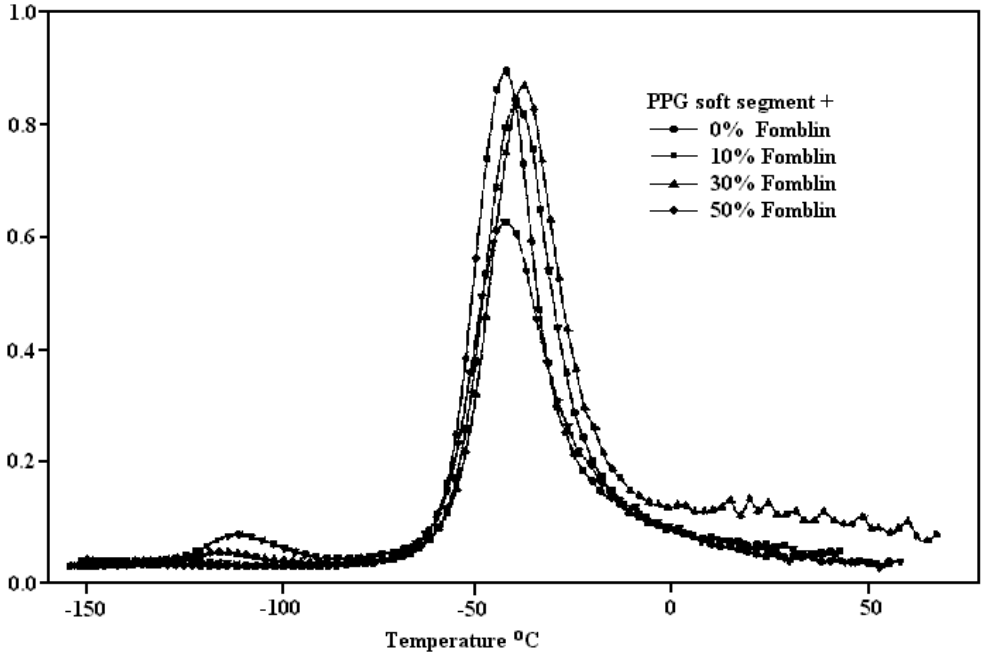


Figure 1.8.5. Fomblin® influence on a PPG soft segment polyurethane. [11]

2. Experimental

The thermal oxidative degradation of fluorinated polyurethane elastomers was assessed in terms of chemical structure, degrees of fluorination and thermal aging. For achieving this goal, the analysis of the changes in chemical structure due to aging was monitored by infrared spectroscopy. In addition, dynamic mechanical analysis (DMA), mass retention (isothermal exposure), contact angle, intrinsic viscosity and thermo gravimetric analysis (TGA) were used for studying the degradation mechanism of the studied polyurethanes and for verifying if the solvent was completely removed in the casting process. The thermal gravimetric analysis also allowed to study the fluorine influence on the onset temperatures of non isothermal degradation of these polyurethanes and the influence of different soft segments on the TGA results.

A flow chart of the experimental procedures and analysis techniques is shown on the next page, on figure 2.1. Each of the experimental procedures was separated in individual sections on this chapter with their laboratory setup.

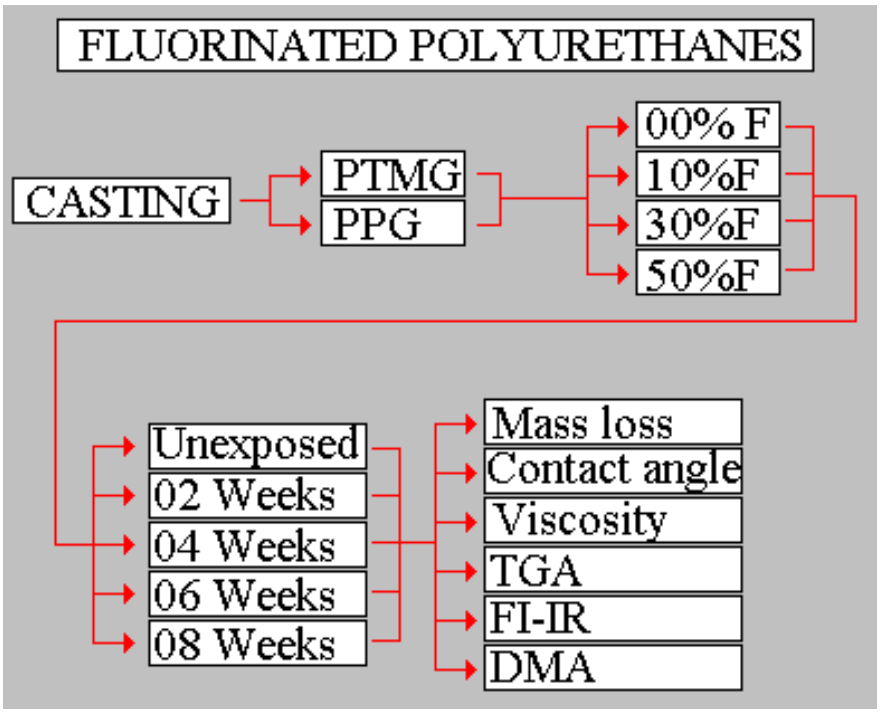


Figure 2.1. Flow chart of the experimental methods.

2.1. Samples

The fluorinated polyurethanes chosen for this project were provided by Hyung-Joong Kim [11] and their chemical structures are described on table 2.1.1. All materials were synthesized by a two step polymerization process, where on the first process the pre-polymer was formed (step called end-capping) and then the chain extender was added for molecular weight increase. The molecular weights and polydispersity [11] of all polymers used and are shown on table 2.1.2.

The catalyst used for the polymerization was dibutyltin dilaurate and the molar ratio used for the components was the following: Diisocyanate: polyether diol:chain extender=2:2:1(molar ratio). A list of all chemicals used on the synthesis of the samples are listed on table 2.1.3. All samples have the hard segment composed of MDI. The PUs are classified according to their soft segment type, being the group A the polyoxypropylene glycol (PPG) samples and group B the polyoxytetramethylene glycol (PTMG). The chain extender used for all samples was ethylene diamine (EDA).

The second step of the polymer synthesis is shown on figures 2.1.1. and 2.1.2. where the circled structures are the chain extenders and the final products are the base polyurethanes. Each of the two groups were synthesized with varying degrees of fluorination, which were obtained by the substitution of the polyglycol by a perfluoro polyether diol (Fomblin Z-DOL®, Mn=1984 from Ausimont, Italy). The chemical structure of Fomblin® is shown on figure 2.1.3. The substitution of the non-fluorinated polyether was done on the first step of the polymerization, or in the pre-polymer formation, when the fluorinated segment was used in place of the base soft segment (PPG or PTMG). If all the base soft segment was replaced by the fluorinated segment, the final polymer would be referred as 100% fluorinated. The percent fluorination used here were 0, 10, 30 and 50%. The general structure of a 50% fluorinated PPG based polymer is shown on figure 2.1.4.

Table 2.1.1. Basic description of the groups molecules.

Group	Hard Segment	Soft Segment	Chain Extender
A	MDI	PPG	EDA
B	MDI	PTMG	EDA

Table 2.1.2. GPC results for the tested materials. [11]

Polymer	**Mw**	**Polydispersity**
PTMG	287,000	1.48
PTMG+10% F	250,000	1.50
PTMG+30% F	180,000	1.52
PTMG+50% F	130,000	1.48
PPG	151,000	2.00
PPG+10% F	224,000	1.60
PPG+30% F	131,000	1.47
PPG+50% F	166,000	1.54

Table 2.1.3. Chemicals used on the synthesis of the samples [11].

	Chemicals	Symbol
Diisocyanate	4,4'-Diphenyl methane diisocyanate	MDI
Polyether diols	Polytetramethylene glycol 2000	PTMG
	Polypropylene glycol 2000	PPG
Chain extender	Ethylene diamine	EDA
Catalyst	Dibutyltin dilaurate	
Solvents	N,N-dimethylacetamide	DMAc
	N,N-dimethylformamide	DMF
	Dimethylsulfoxide	DMSO

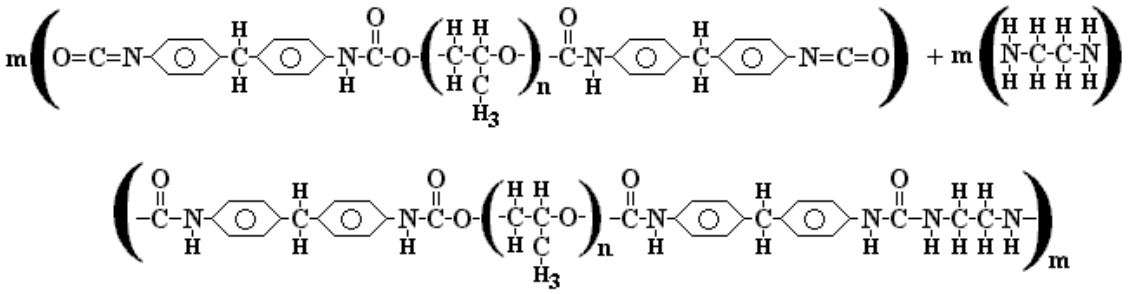


Figure 2.1.1. Second step reaction of synthesis of the PPG based polymer.

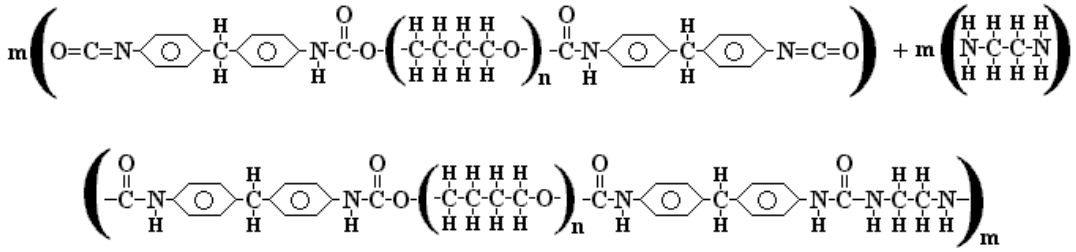


Figure 2.1.2. Second step reaction of synthesis of the PTMG based polymer.

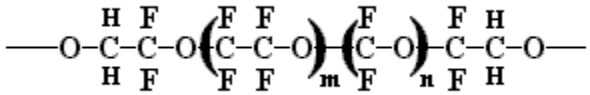


Figure 2.1.3. Chemical structure of Fomblin Z-DOL®.

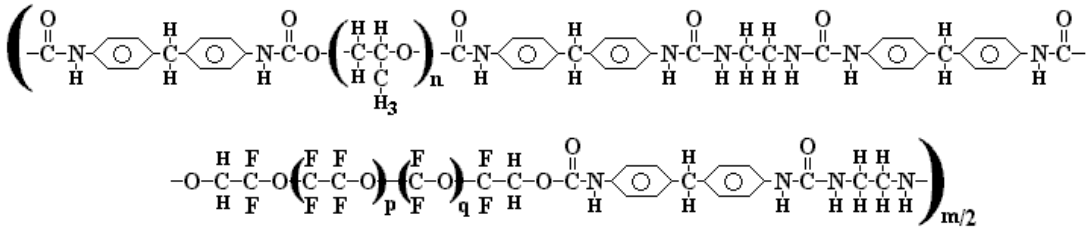


Figure 2.1.4. General chemical structure of a 50% perfluorinated MDI-PPG-EDA polyurethane-urea. The perfluoro segment illustrated is Fomblin Z-DOL 2000® from Ausimont, Italy.

Table 2.1.4. Thickness of samples cast in each of the three molds. Averages in mm.

Sample	Averages - mold one	Averages - mold two
PTMG	0.24	0.14
PTMG+10%F	0.13	0.14
PTMG+30%F	0.10	0.16
PTMG+50%F	0.13	0.15
PPG	0.15	0.22
PPG+10%F	0.14	0.19
PPG+30%F	0.13	0.18
PPG+50%F	0.11	0.15

2.2. Films Preparation

The polymers were dissolved in N,N-dimethyleformamide (DMF) to form a solution having a concentration of 10g/l. The polymers were mixed for approximately 24 hours in a high density polyethylene bottle. Films were solvent cast using a Teflon® mold (4in diameter). The solvent was extracted initially for four hours at 80^{o}C. The films were vacuum dried at 50^{o}C for 24 hours. The thickness of all samples was estimated to be similar by the volume of solution dropped on the mold and are shown on table 2.1.4.

2.3. Thermal Exposure

The thermal exposure was done in a convection oven with a temperature controller at approximately 118±3^{o}C, which accelerates the thermal oxidative process of the polyglycols studied. The samples chosen for exposure were those of thickness closer to 0.15mm, either from mold A or B (section 2.1.). The influence of the thickness is assumed to play an important role on the oxygen access to the core of the samples. During exposure, the samples were frequently switched positions in the oven to uniform exposure and their mass were measured for mass retention analysis. In addition, the

exposure was repeated with smaller samples for collection of mass information and statistical analysis of the results. The mass data was measured in a calibrated 0.0001g balance and the samples were cut in different shapes and sizes for avoiding collection error.

All films were exposed and one quarter of each was extracted every two weeks. This method was chosen for reducing the edge oxidation (more evident in thicker samples) due to the greater oxygen access to the interior of the sample. The samples were extracted by impact cutting for avoiding shear and by creating a clean cut.

2.4. Surface Wettability

Contact angle was performed with a KD Scientific syringe pump model 100, using a B.D. 20ml plastic syringe, with a height of 15 mm from the syringe to the sample's surface. The image captioning was done with a Sony Hi Resolution CCD-Iris color video camera, with 1.5X zoom and automatic back focus. As the image was sent to a computer monitor, the total magnification of the water bubble was approximately 80X. The backlighting (for better contrast) was provided through a Fiber Lite PL-800 and a fiber optics Dolan-Jenner flat desktop light model QVABL. The software used to determine the contact angle was the NIH software version 7.0, connected to the video camera, a VCR, a television screen and a computer through a video card.

The solvent used was distilled water, and the drops volumes were 4 and 8 micro liters (one and two drops of 4ml, respectively). The image of the instant of the drop was first recorded in video format and then the contact angle was determined after 2 seconds of contact. The test set up and parameters are in agreement with the ASTM D5725-99 for surface wettability and absorbency of sheeted materials. Figure 2.4.1. shows a schematic drawing of the setup for the measurement of the contact angles, and a picture of a sample being tested is shown on picture 2.4.2. All surfaces, camera, syringe pump and syringe were leveled before testing.

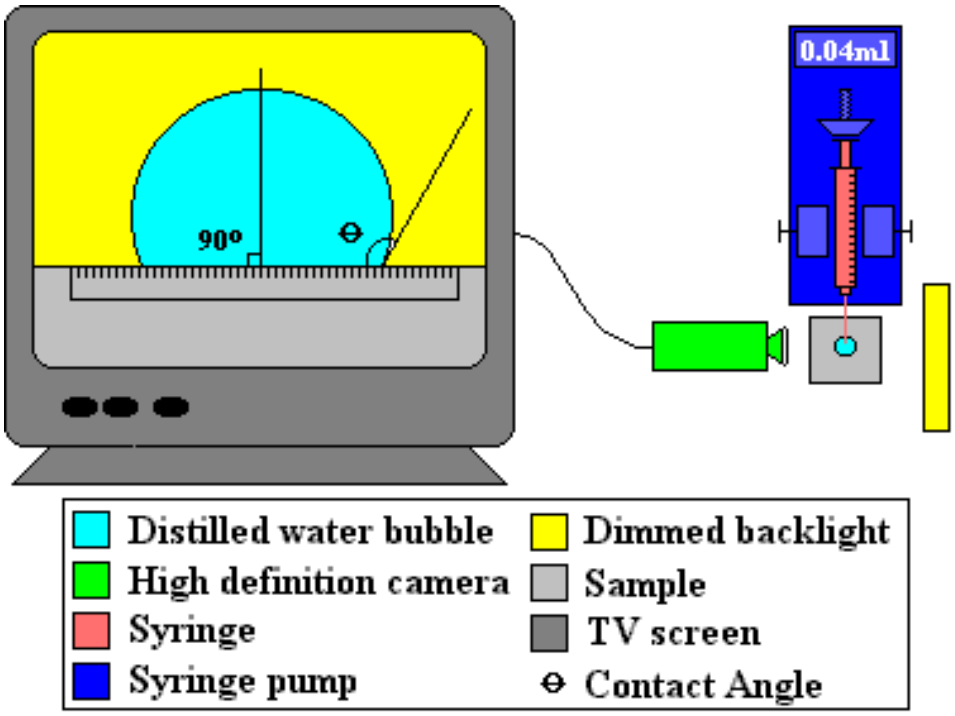


Figure 2.4.1. Setup for wettability measurement.

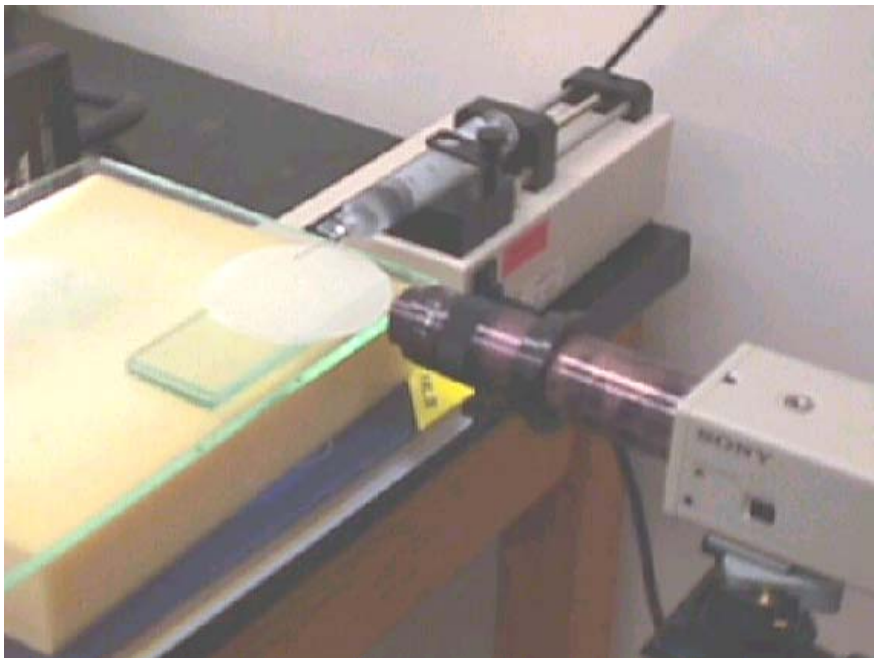


Figure 2.4.2. Contact angle setup, sample, syringe pump and high resolution camera.

2.5. Intrinsic Viscosity

The intrinsic viscosity was determined from efflux times obtained from solutions of different concentrations. The experiments were done with the use of an Ubbelohde viscometer (Canon Instrument Company, model 1 H 901). The solvent used for dissolving the polymers was N,N-dimethylformamide (DMF). The polymers were added to the solvent at an initial concentration of 10g/l. The solution was agitated for 24 hours or until there was no apparent solid residue. The viscometer was checked for impurities by measuring the efflux time of the pure solvent and comparing it to values available on the literature. The efflux times for the solution were measured at 50^{o}C. Three concentrations were used for yield viscosity measurements, by the dissolution of additional 5ml of solvent each time. The temperature chosen for the experiment was 50^{o}C. A cleaning solution was used for eliminating any polymer residue every time a new polymer solution was studied.

A polymer was considered to be insoluble if after one week on the wrist agitator with the solvent there still would be a considerable amount of solid residues in the solution. The intrinsic viscosity on this case is considered to be infinite.

2.6. Thermal Gravimetric Analysis

The thermal gravimetric analyzer used was a Mettler TG50, with the use of a Mettler M series balance and a desktop computer. The software used for the experiment was the TGA TG50. The gas flow used was 4ml/min (nitrogen and air).

An alumina pan was used and fired before the test to assure the absence of contaminants. The balance was reset with the pan inside the instrument and with the gas flow set to the same flow as during the test. The sample's mass was then measured and the test was started. The heat rate used for the tests was 10^{o}C/m, starting at 50 ^{o}C and ending at 500 ^{o}C. A scheme of the TGA analyzer is shown on figure 2.6.1.

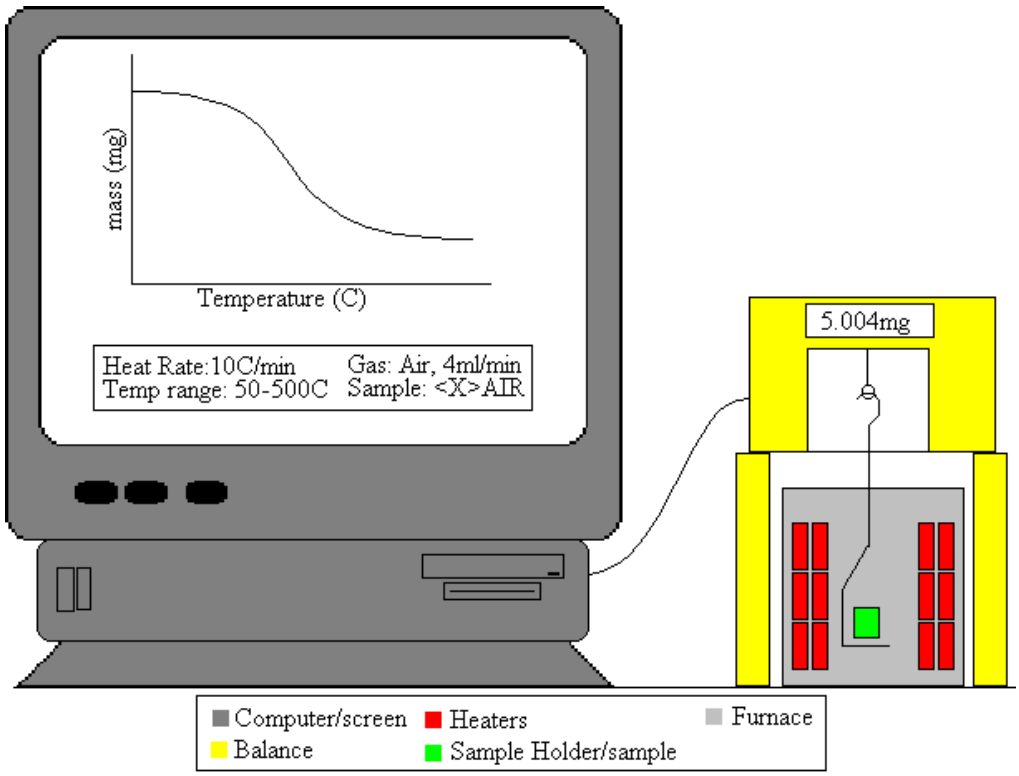


Figure 2.6.1. Setup for TGA analysis.

2.7. infrared Analysis

A BioRad FTS 6000e Infrared Spectrometer equipped with a UMA 500 infrared microscope was used to collect spectra. The software used for analyzing the scans was the IR Winpro® software from BioRad. A total of 1024 scans at a resolution of 4 were the parameters for all tests. The microscope allows the collection of spectrum from selected regions of the samples to be tested. For this work, the microscope is invaluable for the selection of regions of the sample to be tested that are consistent in terms of surface smoothness. An image of the IR/ATR setup is shown on figure 2.7.1.

2.8. Dynamic Mechanical Analysis

A DMTA V from Rheometrics was used for the dynamic mechanical tests (DMA). The test conditions and parameters including strain, pre-load, frequency range, temperature range, temperature ramp, minimum static and dynamic forces, etc. were chosen to be identical for all tests. All parameters are listed on table 2.8.1. and the test setup is illustrated on figure 2.8.1.

The samples that could not withstand the mechanical oscillation of the set test parameters (minimum 5g of dynamic load) were considered to be too degraded for the analysis. On this case, the last exposure period sample that withstood the test was considered to be the lengthiest valid exposure time.

Table 2.8.1. DMA general test parameters.

Thickness	Length	Width	Frequency range	Temperature range	Auto tension	Temperature ramp	Static>dynamic force
~0.1mm	15mm	~6mm	0.01 to 100Hz	-145 to 150^{o}C	Yes,10g	1 ^{o}C /min	10%

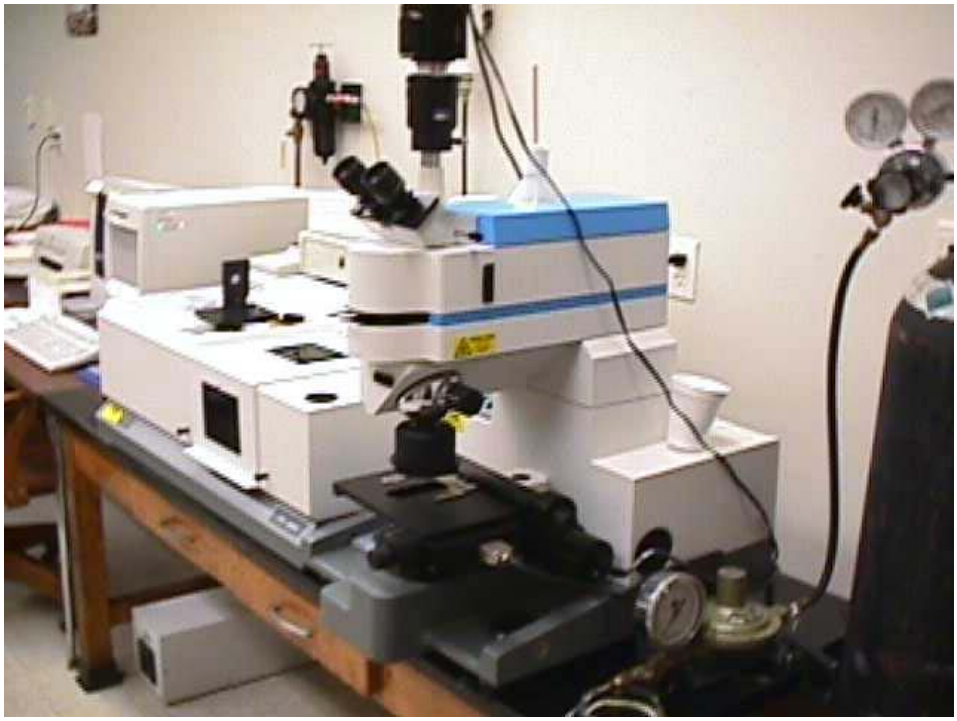


Figure 2.7.1. IR/ATR setup.

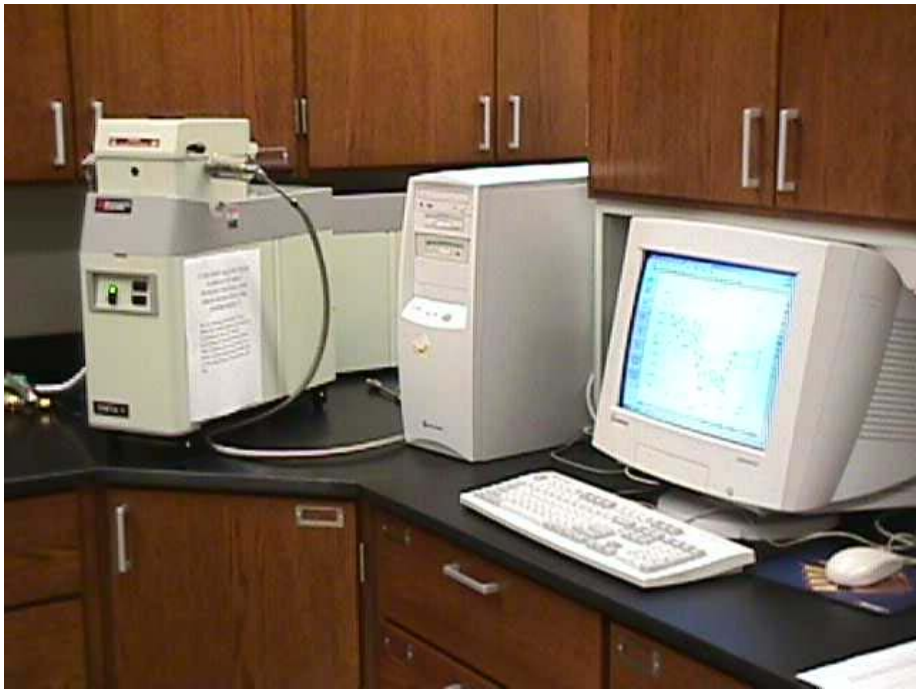


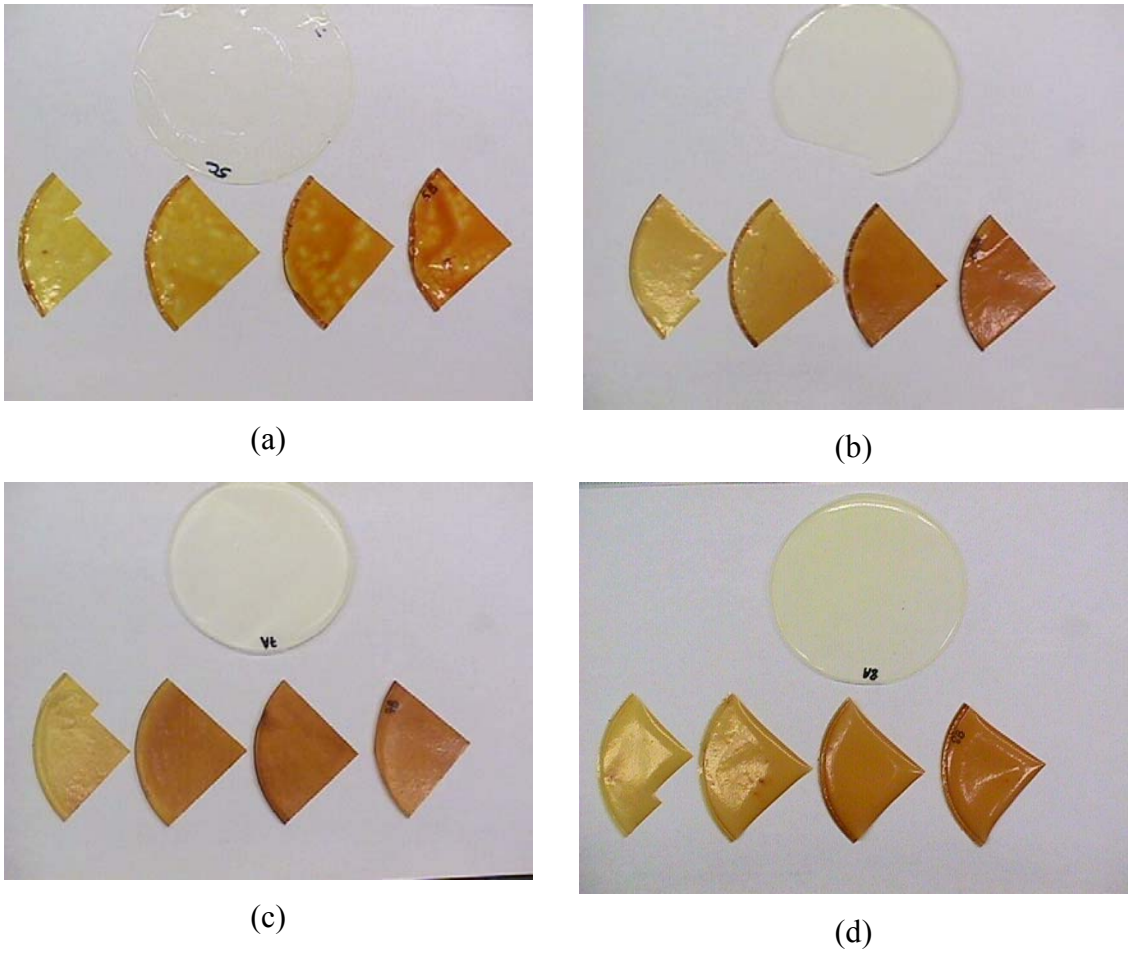
Figure 2.8.1. DMTA V from Rheometrics®.

3. Results

This chapter includes all the experimental results for this work. The results will be commented in general way, but the analysis and correlation to other tests and properties will be included on the discussion chapter. All tests show results of films cast and exposed as described on the experimental chapter, with identical casting parameters. The degradation evaluation will be done according to the chemical and physical properties of the samples, monitored relative to their original chemical structure - for varying percent fluorinated soft segment, for structure of basic non fluorinated soft segment (PPG or PTMG) and to the extent of exposure.

Evidence of the degradation effect on the samples due to exposure times can be seen on figures 3.1. and 3.2. The yellowing is attributed to the formation of quinoid type groups as explained in greater details on section 4.5.1. All samples presented yellowing to some extent after exposure, and the colors reached darker shades with longer exposure times. It is very clear from the images on figures 3.1. and 3.2. that all samples were originally translucent white with no evidence of yellowing. In addition, note the four quarter of circles were taken from the same originally non-exposed circular sample. The PTMG based samples, especially the non-fluorinated samples (figure 3.1.(a)) presented slight non-uniformity in the coloration after exposure. This effect is due to variations on the thickness of this specific sample. As the non-fluorinated PTMG based sample is clear (almost transparent), the thickness variations will induce different shades of yellow/brown with aging, as seen on figure 3.1.(a).

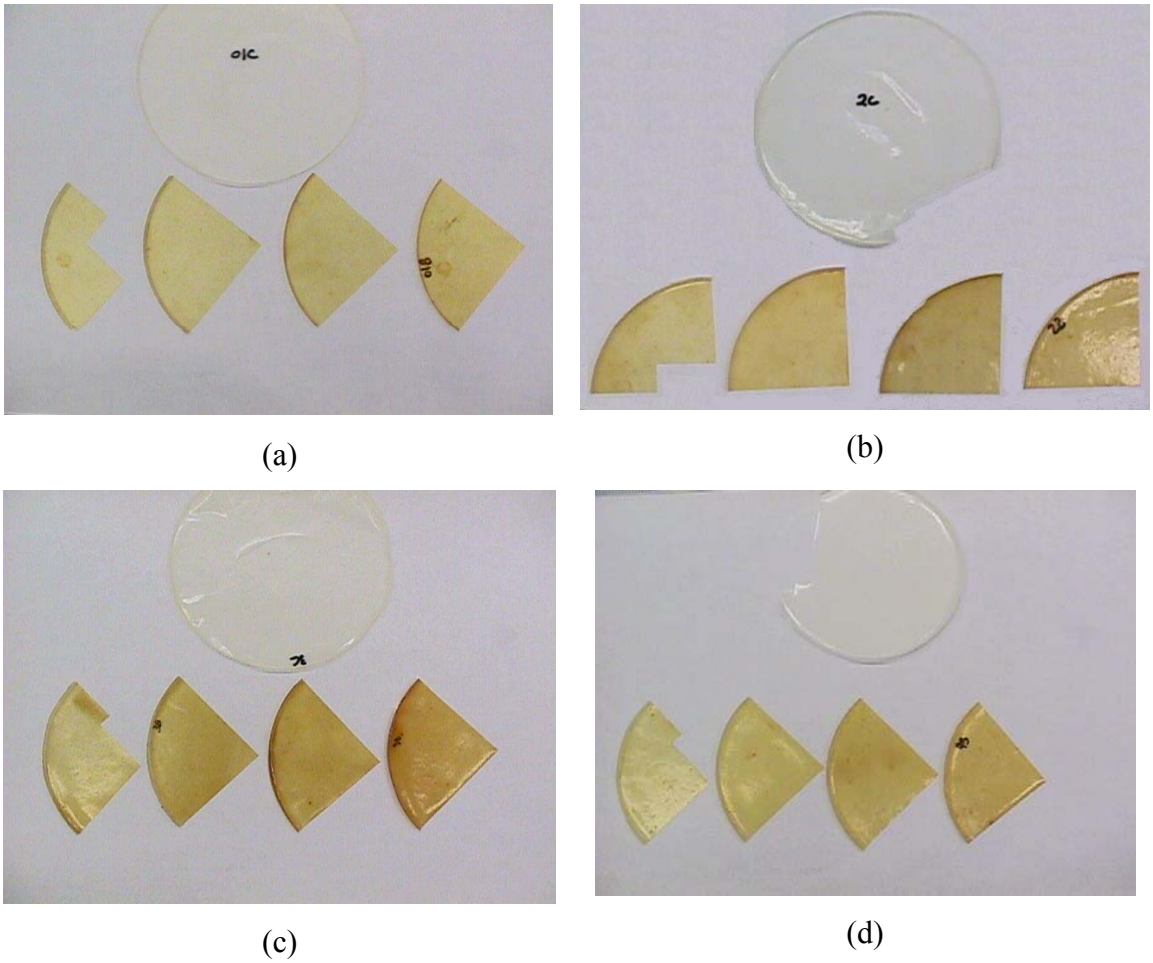
The solubility parameter for each segment (hard and soft) was determined for all studied polyurethanes. The theoretical structures of the polymers were used to calculate the overall volume and cohesive energy for the complete chains and the results are shown on table 3.1.



(a) (b)

(c) (d)

Figure 3.1. PTMG based samples with varying exposure times. (a) Non fluorinated samples, unexposed, and exposed for 02, 04, 06 and 08 weeks, respectively. (b), (c) and (d) are of 10, 30 and 50% fluorinated soft segments.



(a) (b)

(c) (d)

Figure 3.2. PPG based samples with varying exposure times. (a) Non fluorinated samples, unexposed, and exposed for 02, 04, 06 and 08 weeks, respectively. (b), (c) and (d) are of 10, 30 and 50% fluorinated soft segments.

Table 3.1. Estimation of solubility parameters of each component of the studied polymers.

Component	E_{coh} (J/mol)	V (cm^3/mol)	δ(J/cm^3)
EDA	26620	41.2	25.42
MDI	135800	177.9	27.63
PPG 2000	561970	1853.4	17.41
PTMG 2000	627320	1845.2	18.44
Fomblin® 2000	223570	855.6	16.16

The solubility parameters were calculated using equation 1.1.1. and the values are tabulated on table 1.1.1. The solubility parameters of the hard segment (MDI and chain extender (EDA)) are very different from the ones from the soft segments (PPG and PTMG).

The substantial difference between the hard and soft segments solubility parameters implies in incompatibility. The difference between the solubility parameters between the non fluorinated and the fluorinated segments is small. Thus, the two soft segments would tend to mix and affect the morphology of the polymer.

3.1. Thermal Exposure: Mass Loss

The mass loss results were obtained from the measurement of samples residual mass averages according to their initial weight. The results (figure 3.1.1.) illustrate the effect of fluorination on the studied PTMG based PUs. With increasing fluorination, the PTMG based PUs presented an increasing tendency of loosing mass. The same was observed for the PPG based polyurethanes (figure 3.1.2.).

When comparing the two different soft segments polyurethanes, the PTMG based polyurethanes presented better mass retention properties than PPG based polyurethanes with aging, as illustrated on figure 3.1.3. The maximum mass loss was of approximately 7% loss of original weight, for the 50% fluorinated PTMG based sample (figure 3.1.1.).

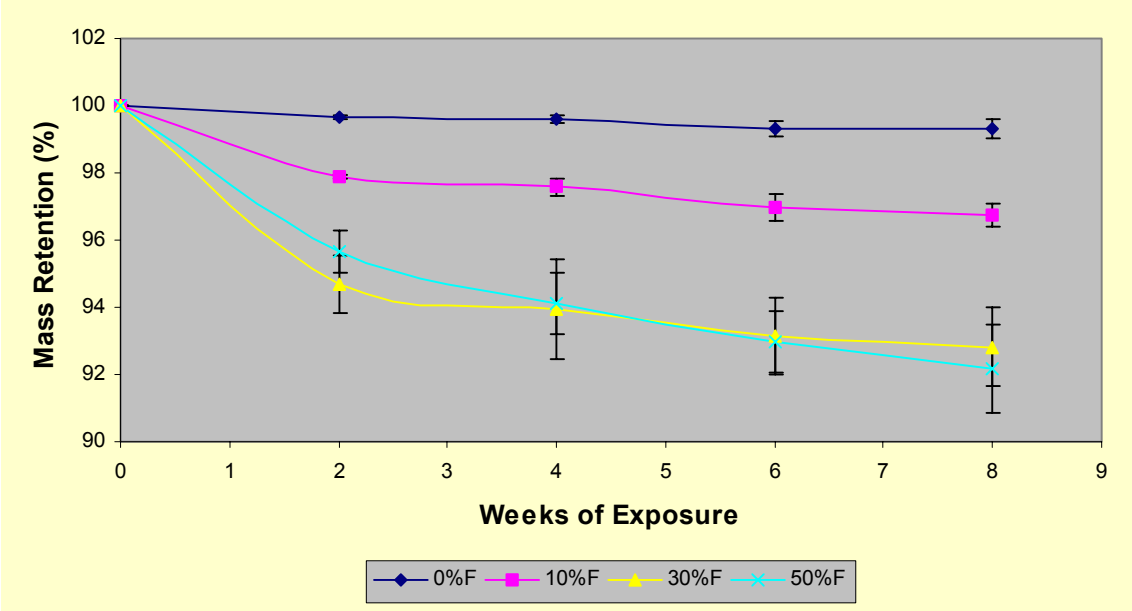


Figure 3.1.1. Mass retention of PTMG based polyurethanes.

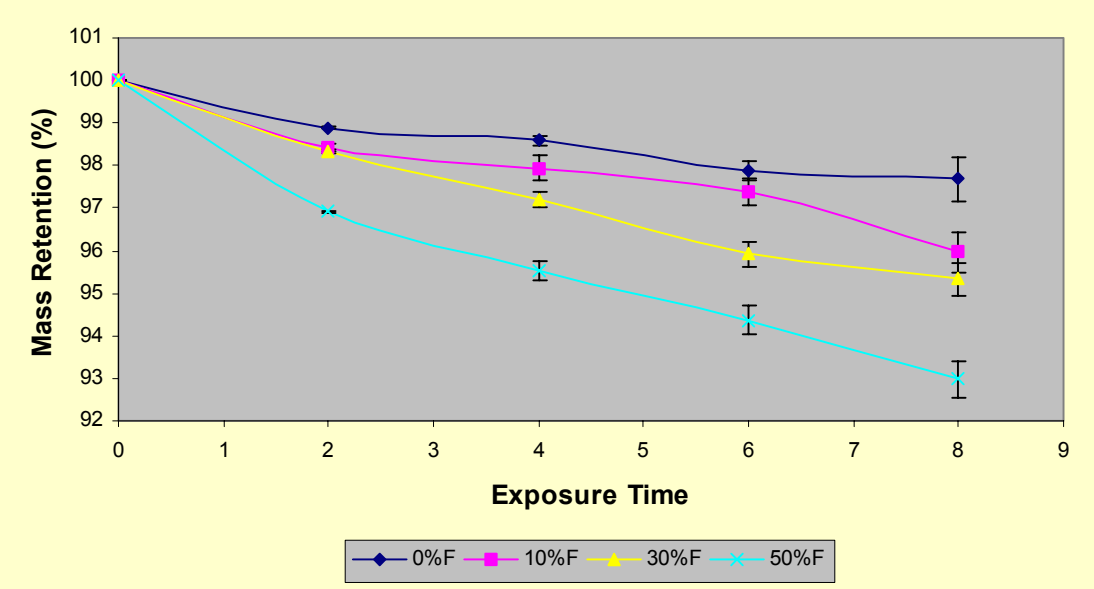


Figure 3.1.2. Mass retention of PPG based polyurethanes.

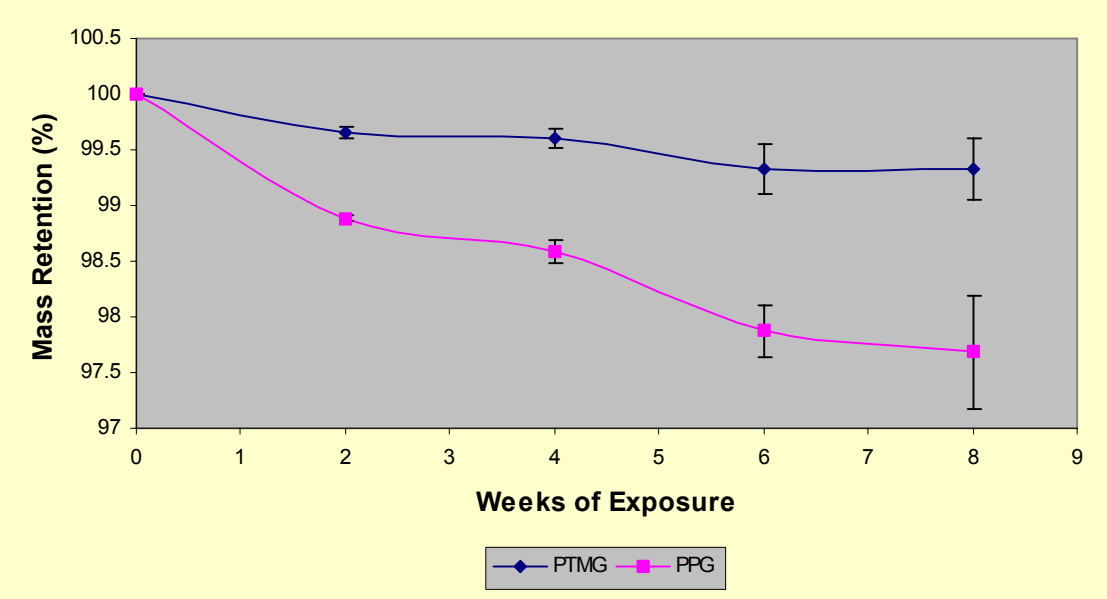


Figure 3.1.3. Mass retention of non fluorinates polyurethanes.

Figures 3.1.1. to 3.1.3. show an increasing tendency for the error for the increasing exposure times. This effect may be due to a small difference in mass loss tendency for each individual sample. A small difference in mass loss is expected for samples due to thickness variation, once the degradation process involves oxygen diffusion (thermo-oxidation). The causes of this effect and its correlation to the chemical structure and other test results will be further explored in the discussion chapter.

3.2. Surface Wettability – Contact Angle Measurements

Increasing degrees of fluorination in general increases the contact angles of the PTMG based PUs studied. Aging does not significantly change the contact angles of the PTMG based PUs, although the 50% fluorinated polymer reduced its contact angle more than the others (figure 3.2.1.). The PPG based PUs (like the PTMG based polymers) presented an increase in contact angle with increasing degrees of fluorination. Surprisingly, aging increased the hydrophobic behavior of the PPG based PUs (figure 3.2.2.). The comparison of the PTMG and PPG based PUs show the slightly higher contact angles values of the PTMG based PUs. (figure 3.2.3.)

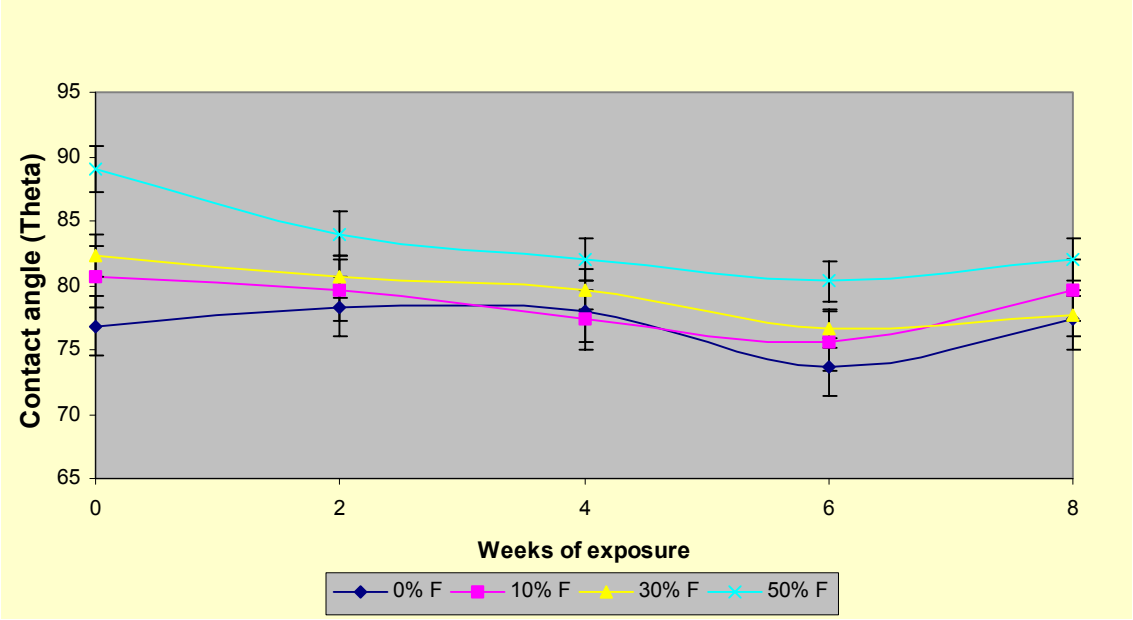


Figure 3.2.1. Contact angle of PTMG based samples versus exposure time.

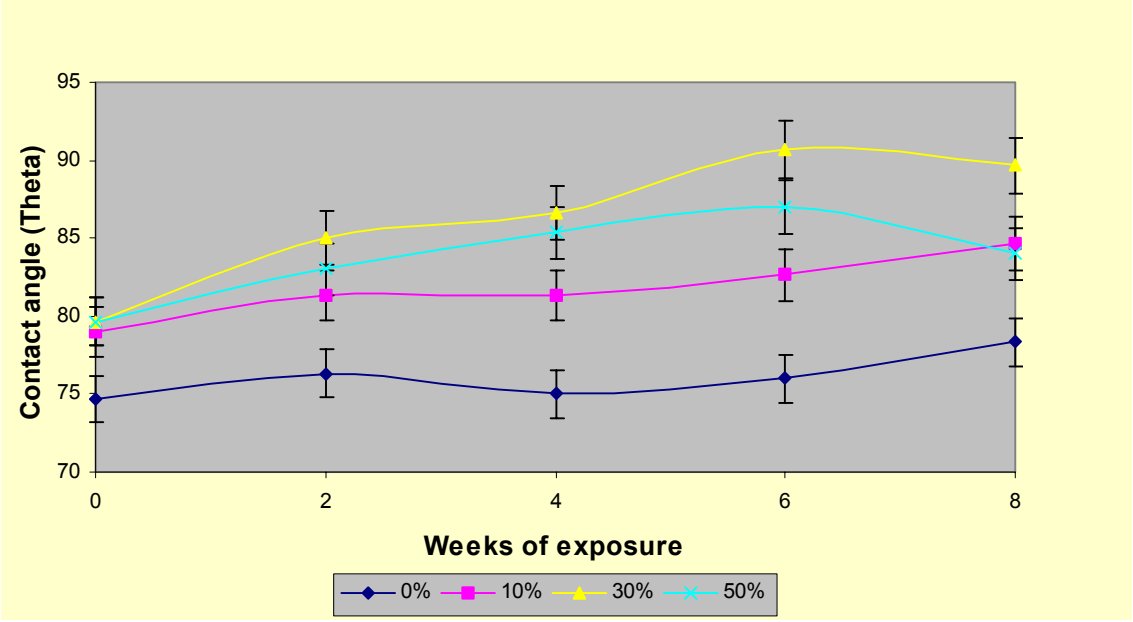


Figure 3.2.2. Contact angle of PPG based samples versus exposure time.

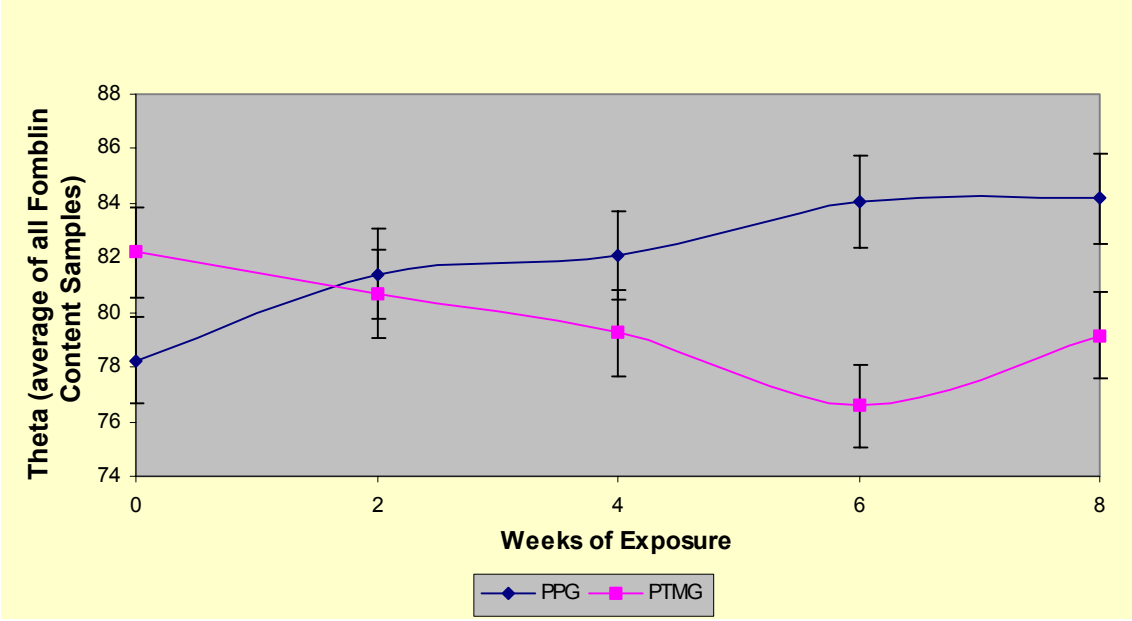


Figure 3.2.3. Average contact angles for each group of samples versus exposure times.

3.3. Intrinsic Viscosity

Intrinsic viscosity was determined from efflux times of solutions of different concentrations. The solvent used was DMF and tests were done at 50°C. None of the exposed PTMG based samples dissolved in the solvent. The extract and gel fraction of these samples were used for infrared analysis.

The efflux time of the pure solvent was used in the equations 1.5.1. to 1.5.4. to calculate the reduced and inherent viscosities. The extrapolation of the reduced and inherent viscosities should coincide at zero concentration (x=0 in the figures of this section) if the results are consistent, the common viscosity value extrapolated is defined as the intrinsic viscosity of the sample. Longer efflux times imply in higher viscosity for the same test conditions. Reductions in efflux times associated with degradation are generally attributed to chain scission mechanism. Crosslinking or even hydrogen bonding drastically increases the efflux times up to infinite values. Crosslinking reduces the ability of the polymer to dissolve in solution, as happened for the PTMG samples.

The results of the intrinsic viscosity analysis are summarized on table 3.3.1. and they show the relevance of the type of soft segment on the viscosity of polyurethanes. The non-fluorinated unexposed PTMG based polyurethanes have much higher values of viscosity than the non-fluorinated unexposed PPG based polyurethane (226% higher). The intrinsic viscosity is directly related to the molecular weight of the polymer. The higher the molecular weight, the slower the solution will flow. The molecular weight of the studied polymers are shown on table 2.1.2.

The degree of fluorination, in general, reduced the efflux times of the polymer, and this reduction is shown in the viscosity values on table 3.3.1. While for the PTMG based polymer the viscosity dropped sharply (from 0.093 to 0.036) with increasing degrees of fluorination, the viscosity dropped comparatively less for the PPG based polymers (from 0.041 to 0.031).

The effect of the different soft segments on the polyurethanes are shown on figures 3.3.1. and 3.3.2., and the symbols used on the captions of this section's figures are summarized on table 3.3.2. The effect of fluorination on the viscosity of all tested polymers can be seen on figures 3.3.1. and 3.3.3.

Aging generally reduces the viscosity of polymers in solution, especially when chain scission occurs during the degradation process. When crosslinking or hydrogen bonding occurs, on the other hand, the viscosity may go up sharply and easily make the sample insoluble, the case of the PTMG based polyurethanes.

The non-fluorinated PPG based polyurethane showed a sharp drop in viscosity after aging (from 0.041 to 0.025). As the degree of fluorination increased, the viscosity drop after exposure is reduced significantly for the PPG based polymers, as illustrated on figures 3.3.3. to 3.3.6. (summarized on table 3.3.3.).

Table 3.3.1. Calculated intrinsic viscosities.

% fluorinated soft segment	PTMG based Unexposed	PPG based Unexposed	PPG based 08 weeks
0	0.093	0.041	0.025
10	0.091	0.060	0.032
30	0.049	0.047	0.040
50	0.036	0.031	0.031

Table 3.3.2. Symbols used on intrinsic viscosity graphs.

Symbol		Symbol	
R	Reduced viscosity	03	PPG based, 30% Fomblin®
I	Inherent viscosity	04	PPG based, 50% Fomblin®
0w	Unexposed	05	PTMG based, 0% Fomblin®
8w	Exposed for 8 weeks	06	PTMG based, 10% Fomblin®
Linear	Extrapolation of curves	07	PTMG based, 30% Fomblin®
01	PPG based, 0% Fomblin®	08	PTMG based, 50% Fomblin®
02	PPG based, 10% Fomblin®		

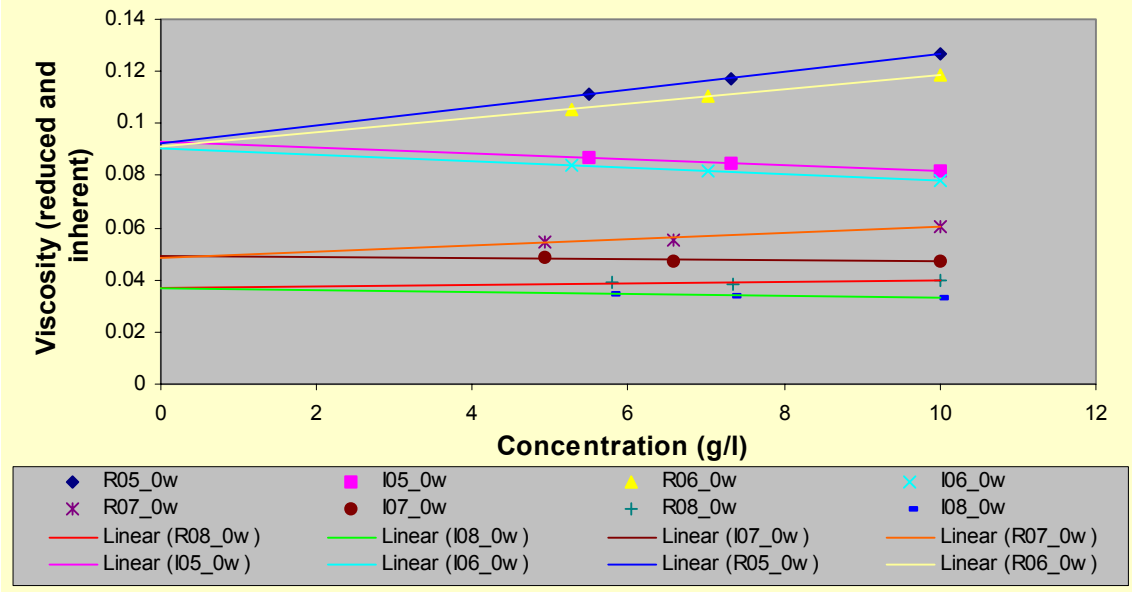


Figure 3.3.1. Intrinsic viscosities of unexposed PTMG based polymers.

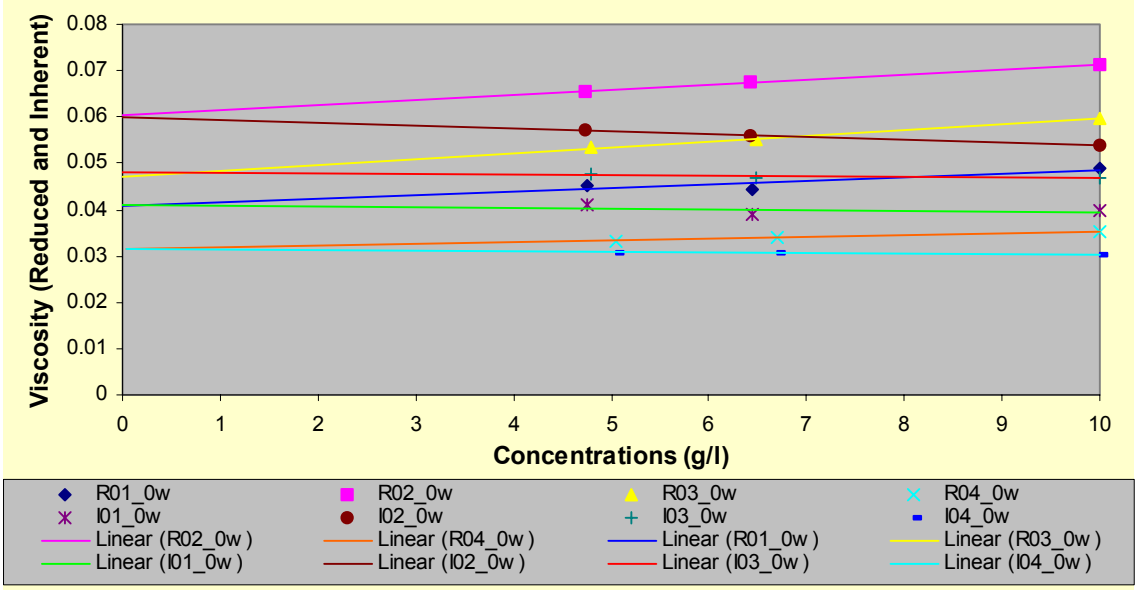


Figure 3.3.2. Intrinsic viscosities of unexposed PPG based polymers.

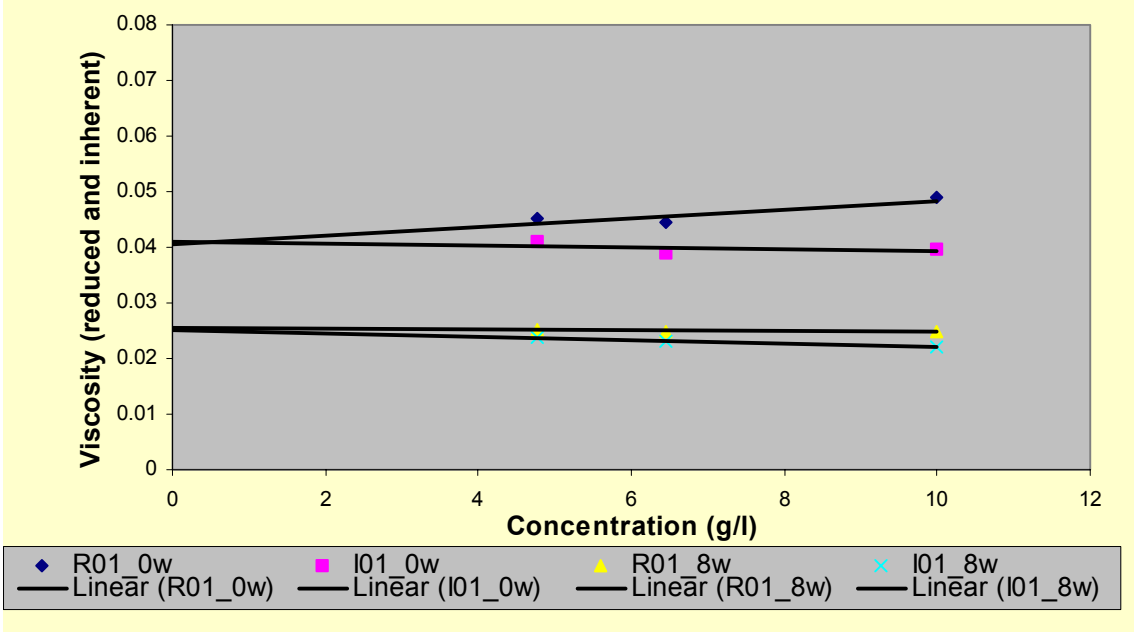


Figure 3.3.3. Intrinsic viscosity of non fluorinated PPG based sample before and after 08 weeks of exposure.

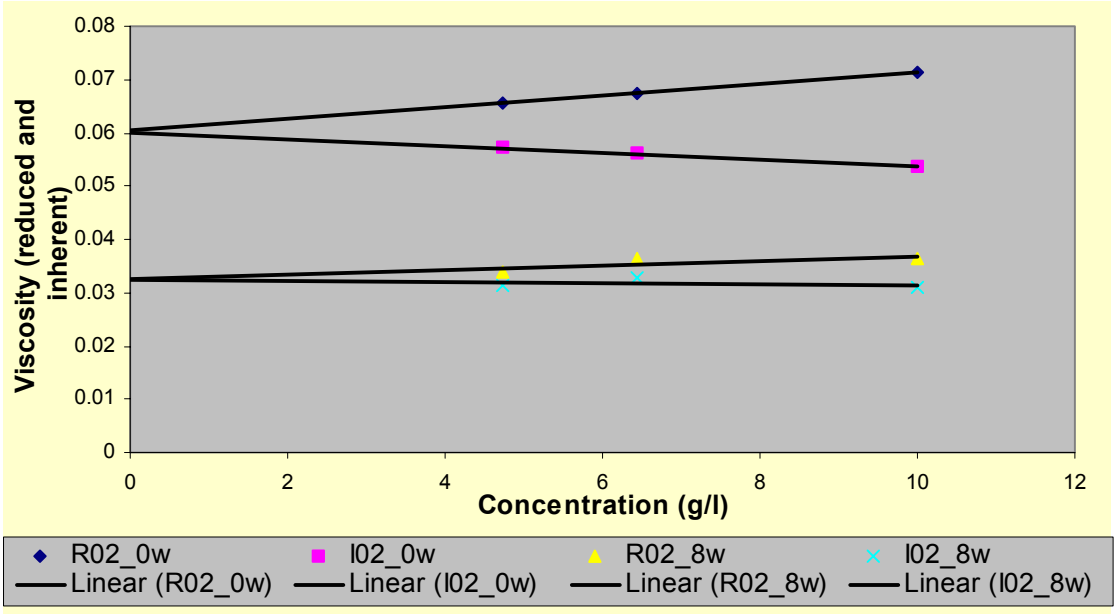


Figure 3.3.4. Intrinsic viscosity of 10% fluorinated PPG based sample before and after 08 weeks of exposure.

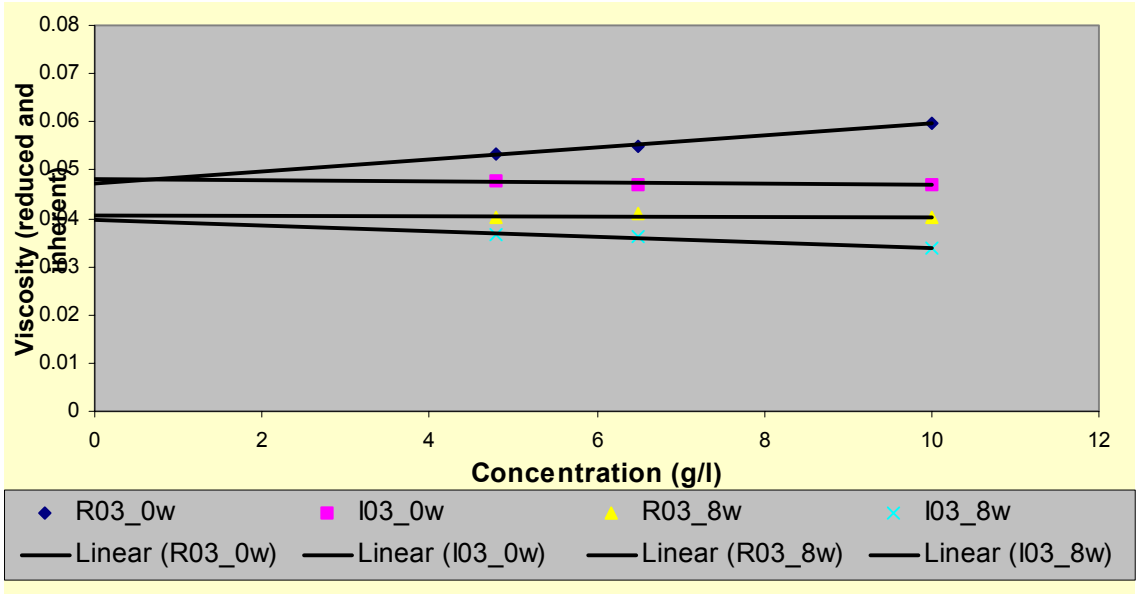


Figure 3.3.5. Intrinsic viscosity of 30% fluorinated PPG based sample before and after 08 weeks of exposure.

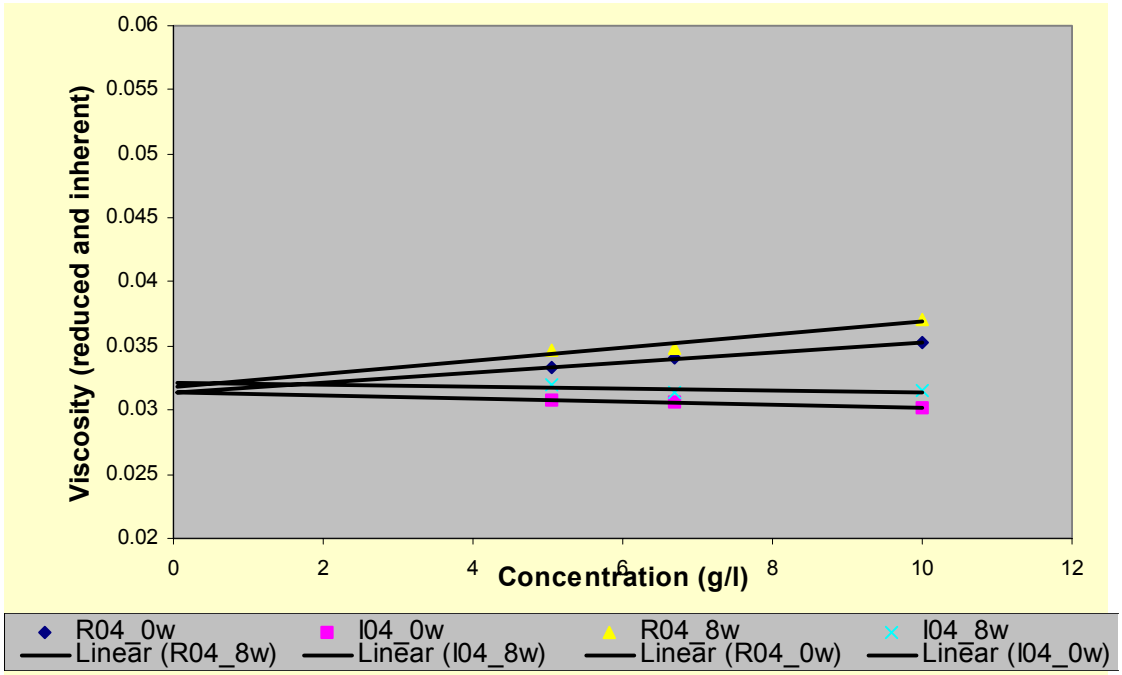


Figure 3.3.6. Intrinsic viscosity of 50% fluorinated PPG based sample before and after 08 weeks of exposure.

Table 3.3.3. Drop in viscosity of PPG based polymers due to exposure.

% fluorinated soft segment	Viscosity drop after exposure
0	39%
10	47%
30	15%
50	00%

3.4. Thermal Gravimetric Analysis

Thermo-gravimetric curves of the unexposed samples were obtained mainly for verifying the effectiveness of the residual solvent removal process and study of the degradation onset temperatures of the studied polyurethanes. For this purpose air flow was used to allow oxidative degradation during testing. Results show the influence of the soft segments and the degree of fluorination (Fomblin® substitutes) on the thermo-oxidative degradation on the studies polyurethanes. Figure 3.4.1. compares the thermal gravimetric behavior of the non-fluorinated and unexposed PTMG and PPG based polyurethanes. While for the PPG based sample the mass loss rate was much higher, the onset temperature of PPG was comparable to that of the PTMG based polyurethane.

The presence of perfluorinated groups in the polyurethanes chains promote changes in the thermal degradation kinetics, as illustrated on figures 3.4.2. and 3.4.3. While the onset temperature of degradation is lowered with increasing degrees of fluorination, the temperature range which the sample looses mass is widened. In addition, for the fluorinated PTMG based PUs (figure 3.4.2.) the mass loss occurs in steps as illustrated on curve D of figure 1.6.2.(a). While the fluorinated PPG based PUs (figure 3.4.3.) mass loss occurs in a single smooth descent as illustrated on curve C of figure 1.6.2.(a). Appendix A contains individual curves for the PTMG and PPG based PUs with varying degrees of fluorination. The determined values of onset, end and maximum reaction rate temperatures for all polymers studied are listed on table 3.4.1. Results show the effect of fluorination on PTMG based PUs. The results for the temperature determined from TGA results are discussed in details on the discussion chapter.

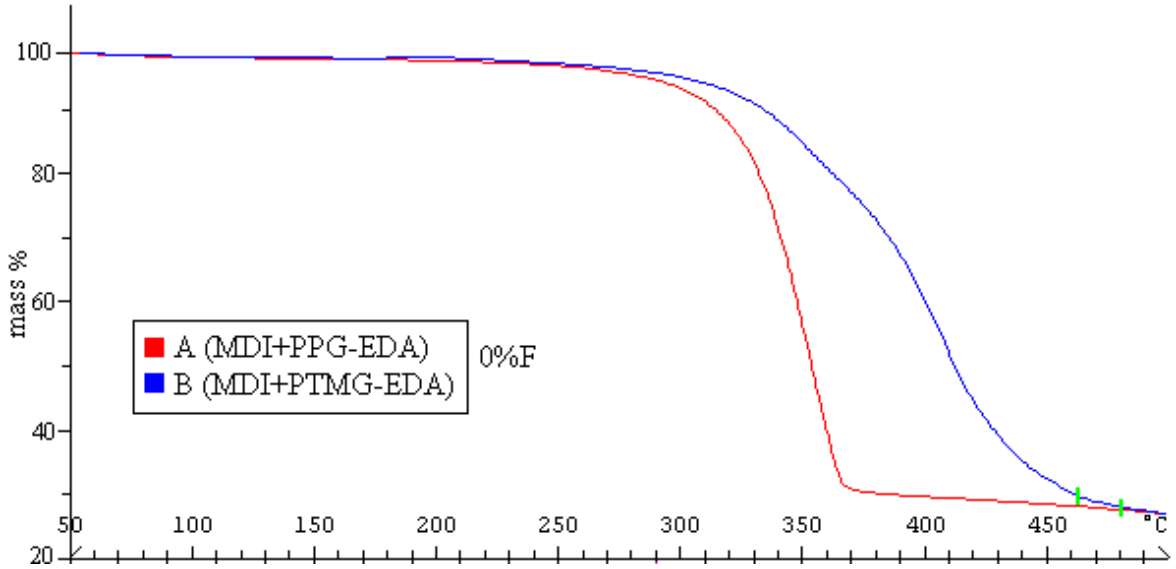


Figure 3.4.1. PPG and PTMG based polymers, non-fluorinated soft segments, unexposed.

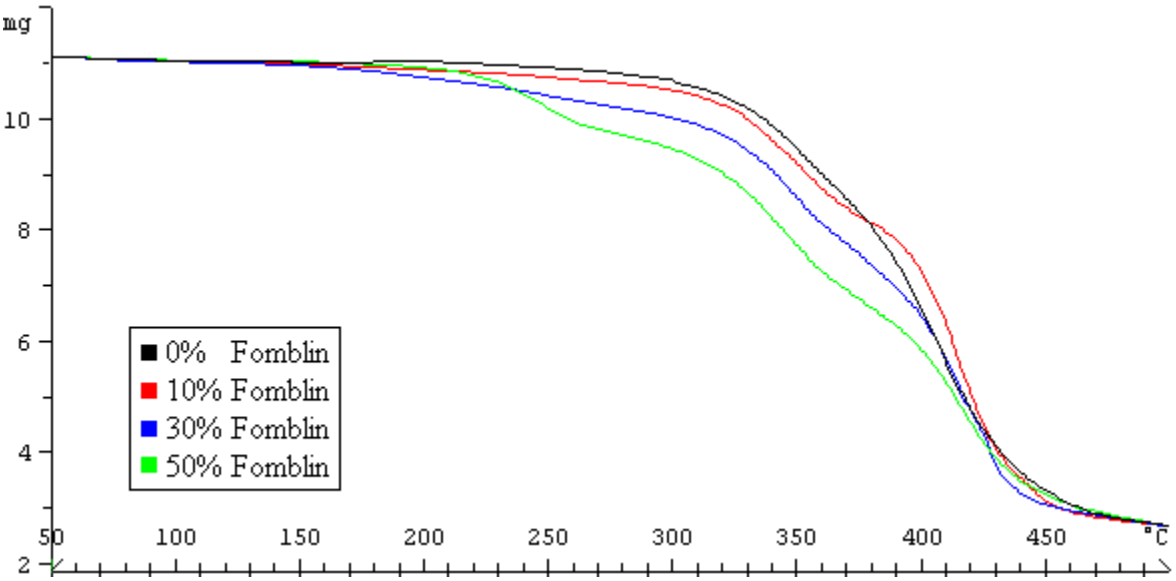


Figure 3.4.2. PTMG based polymers for varying fluorine content, unexposed.

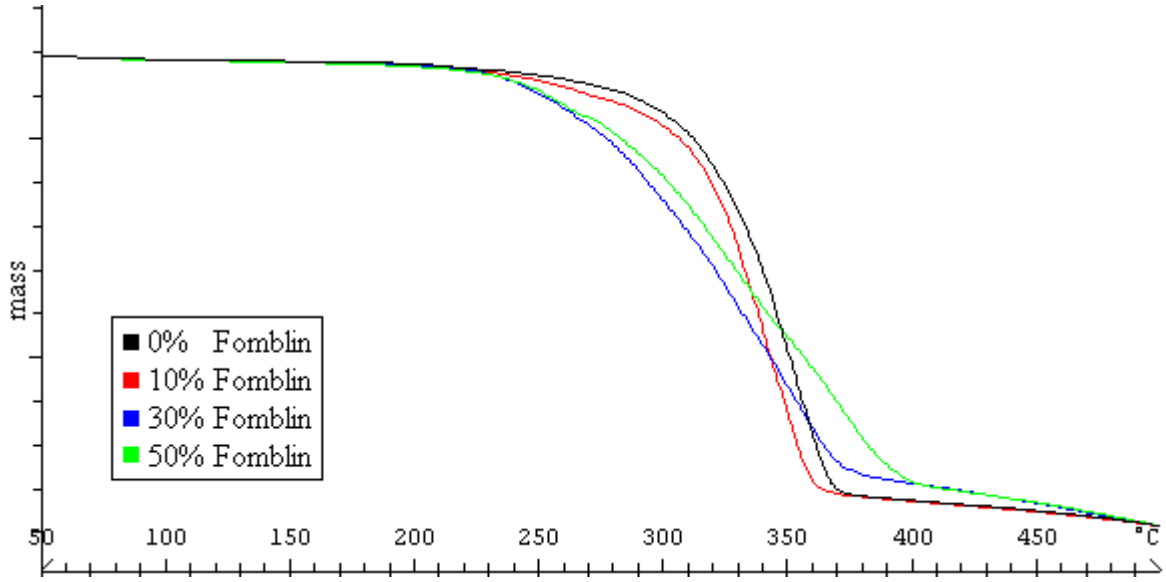


Figure 3.4.3. PPG based polymers for varying fluorine, unexposed.

Table 3.4.1. Onset, end and highest reaction rate of the studied PUs' TGA.

Type	Onset	End	Onset	End	Onset	End	C1	C2	C3
PTMG									
0	323	gradual	gradual	389	389	438	355	gradual	412
10	319	gradual	gradual	376	398	438	350	gradual	418
30	321	gradual	gradual	gradual	403	438	368	gradual	421
50	225	259	320	358	402	439	242	341	419
PPG									
0	325	368	X	X	X	X	345	X	X
10	309	359	X	X	X	X	333	X	X
30	270	371	X	X	X	X	318	X	X
50	270	393	X	X	X	X	331	X	X

3.5. Infrared Analysis

This section includes the spectra of the unexposed and exposed for eight weeks samples, as well as the non-fluorinated and 50% fluorinated samples for PTMG and PPG based polyurethanes. The spectra of all polymers tested according to different soft segment, degree of fluorination and exposure times are shown individually in Appendix B. Composite spectra and relative absorption curves according to degrees of fluorination and exposure times are shown on the discussion chapter.

The assignments for the absorption bands presented on this work are listed on table 1.7.1. This information will be used to interpret the changes on the absorptions according to their ratios to a constant band. The results were analyzed according to the degree of fluorination and the exposure time of the PTMG and PPG based polyurethanes. The reference absorption band used for rationing the absorptions of the PTMG and PPG polymers was the 2860cm^{-1}, attributed to C-H stretching, assumed constant along the exposure times of the studied polyurethanes.

The results show substantial increase in the intensity in the carbonyl region, both for the free and H-bonded (1710 and 1730cm^{-1} shown with an arrow on figures 3.5.1. to 3.5.8.). The carbonyl absorptions as a function of the exposure time are also shown on figures 3.5.1. to 3.5.8. In addition, changes in the MDI regions for the benzene rings illustrate the effect of aging in the polyurethanes, i.e. yellowing, represented by an increase in relative absorption of the 1600 and 820cm^{-1} regions, especially for the PTMG based polyurethanes. Note that the absorption increases substantially with the degree of fluorination on the 820 and 1600cm^{-1} wavenumbers, in special for the PTMG based polyurethanes along aging, attributed to changes in the benzene rings of these polymers. More details on the changes in the MDI structure (and benzene) due to aging will be shown in the discussion chapter (section 4.5.).

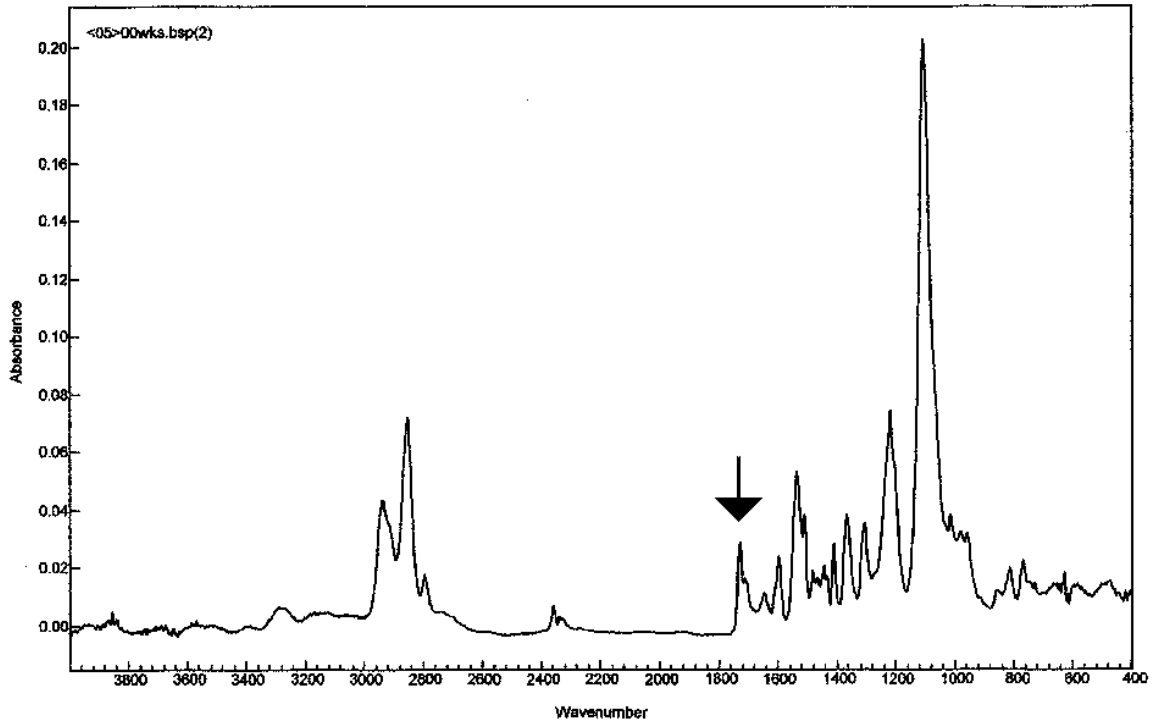


Figure 3.5.1. PTMG based polymer, 0% fluorinated, unexposed.

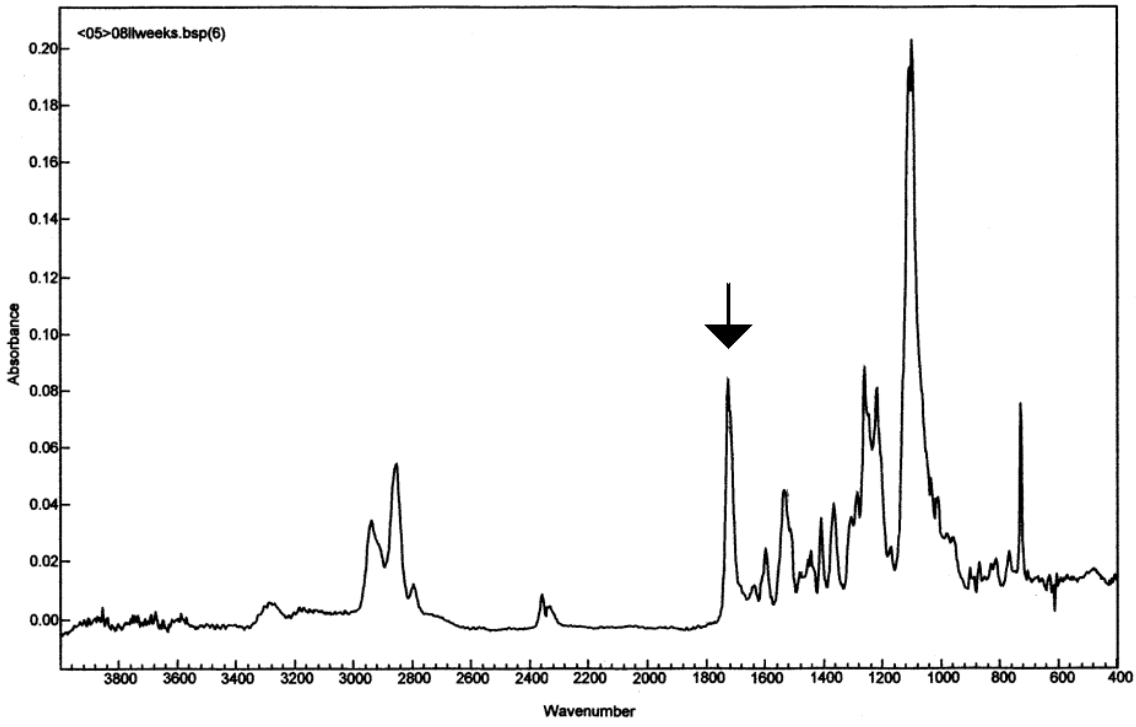


Figure 3.5.2. PTMG based polymer, 0% fluorinated, exposed for 08 weeks.

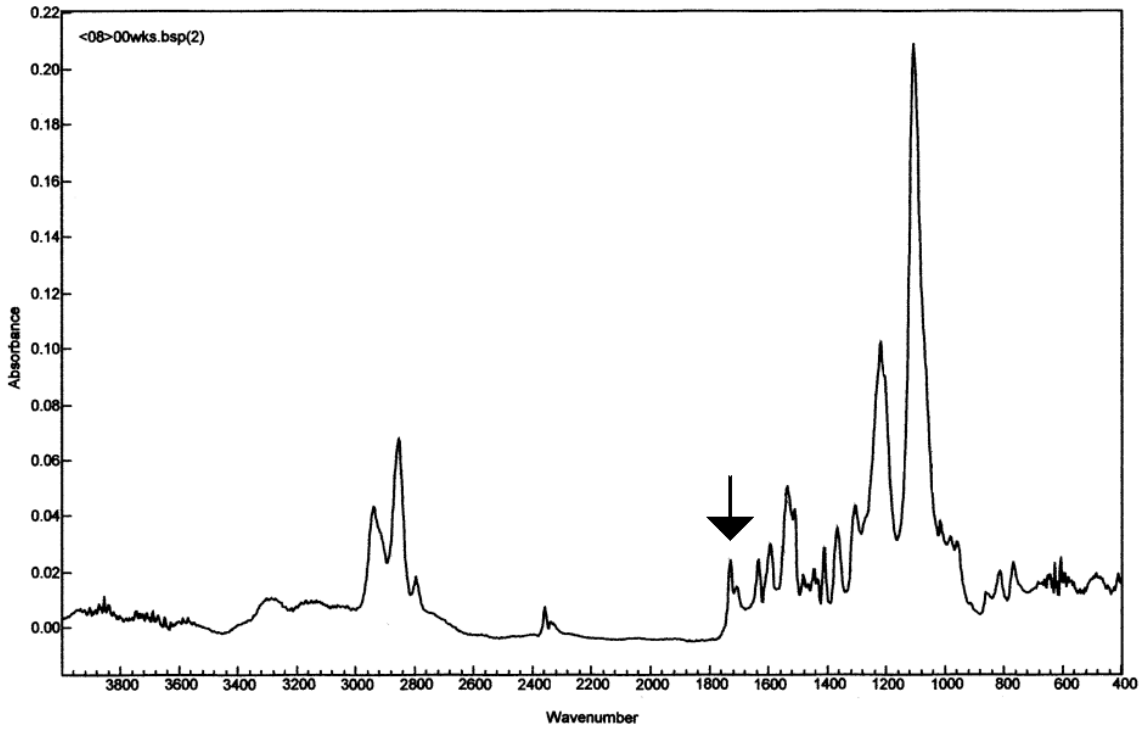


Figure 3.5.3. PTMG based polymer, 50% fluorinated, unexposed.

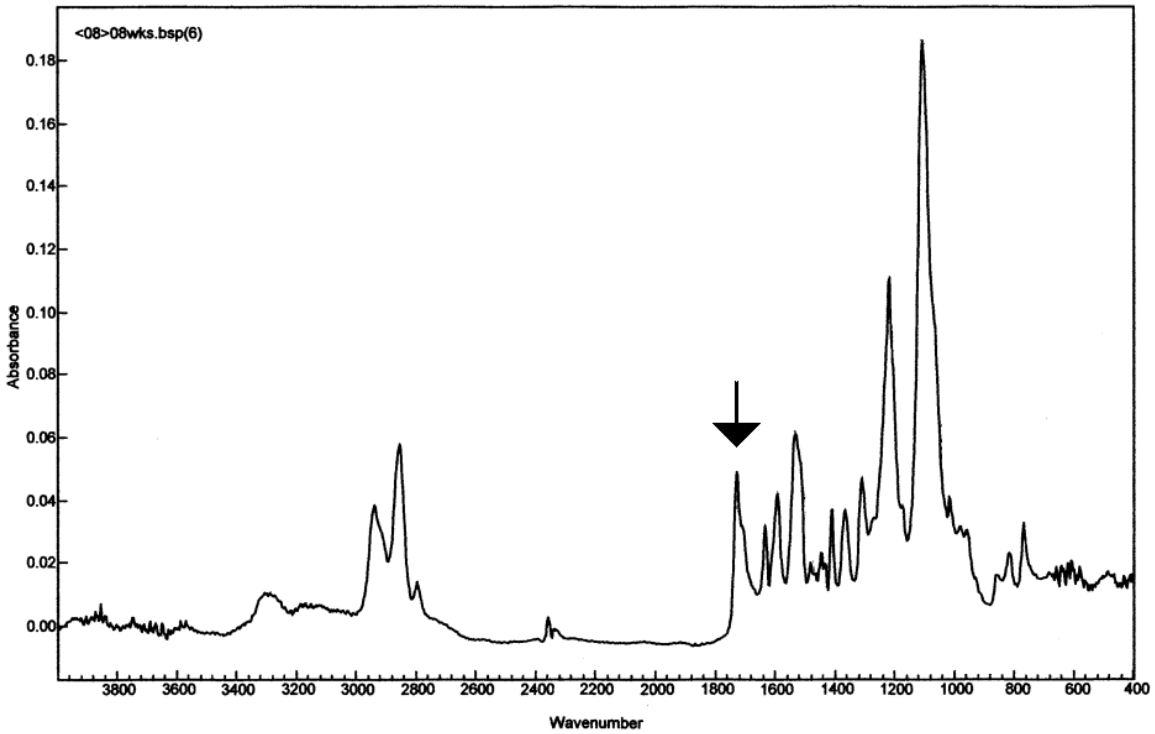


Figure 3.5.4. PTMG based polymer, 50% fluorinated, exposed for 08 weeks.

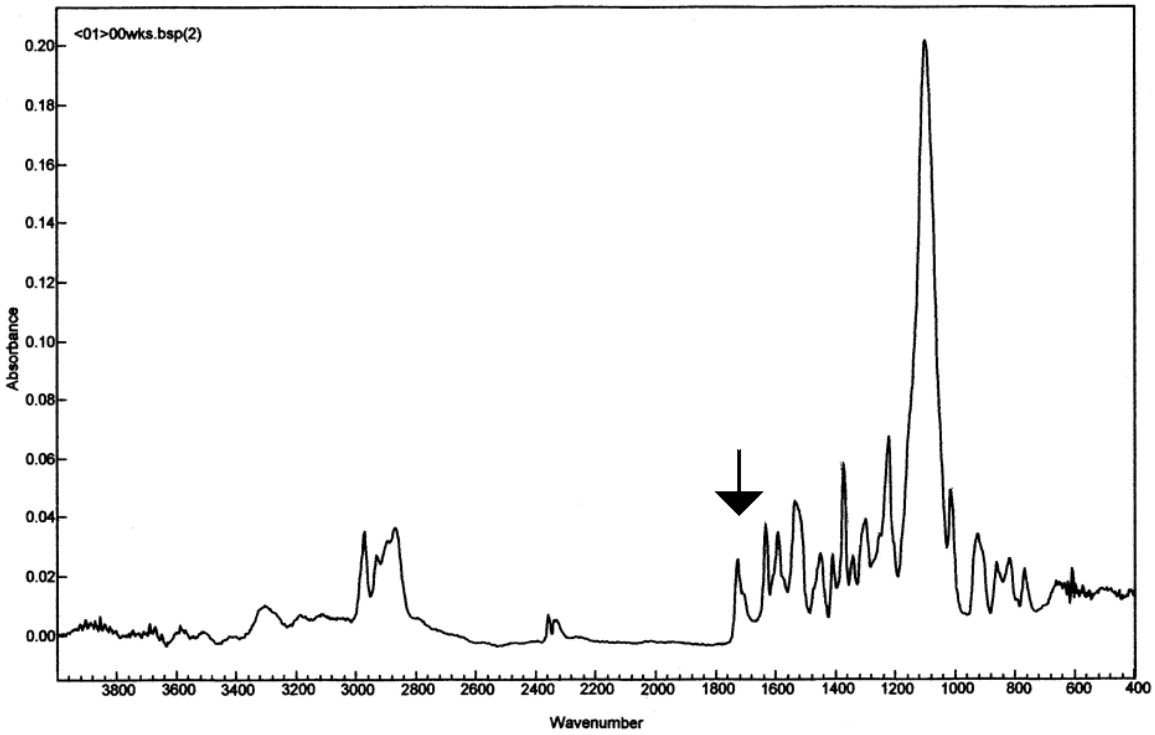


Figure 3.5.5. PPG based polymer, 0% fluorinated, unexposed.

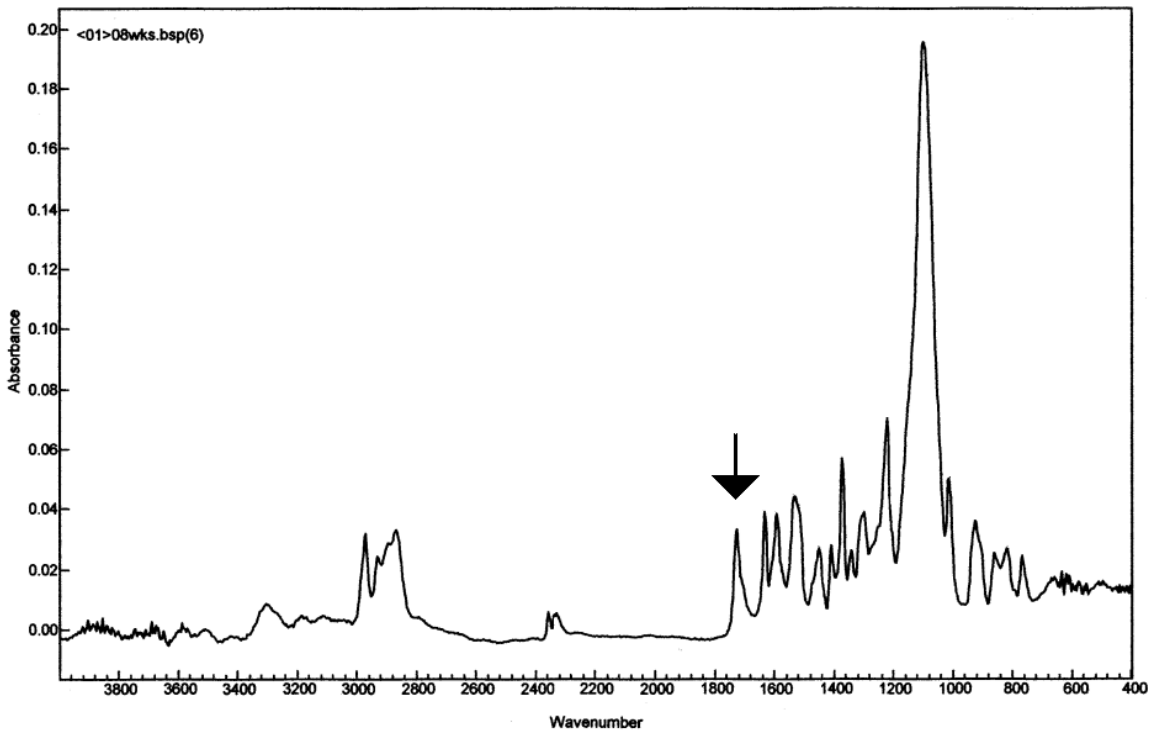


Figure 3.5.6. PPG based polymer, 0% fluorinated, exposed for 08 weeks.

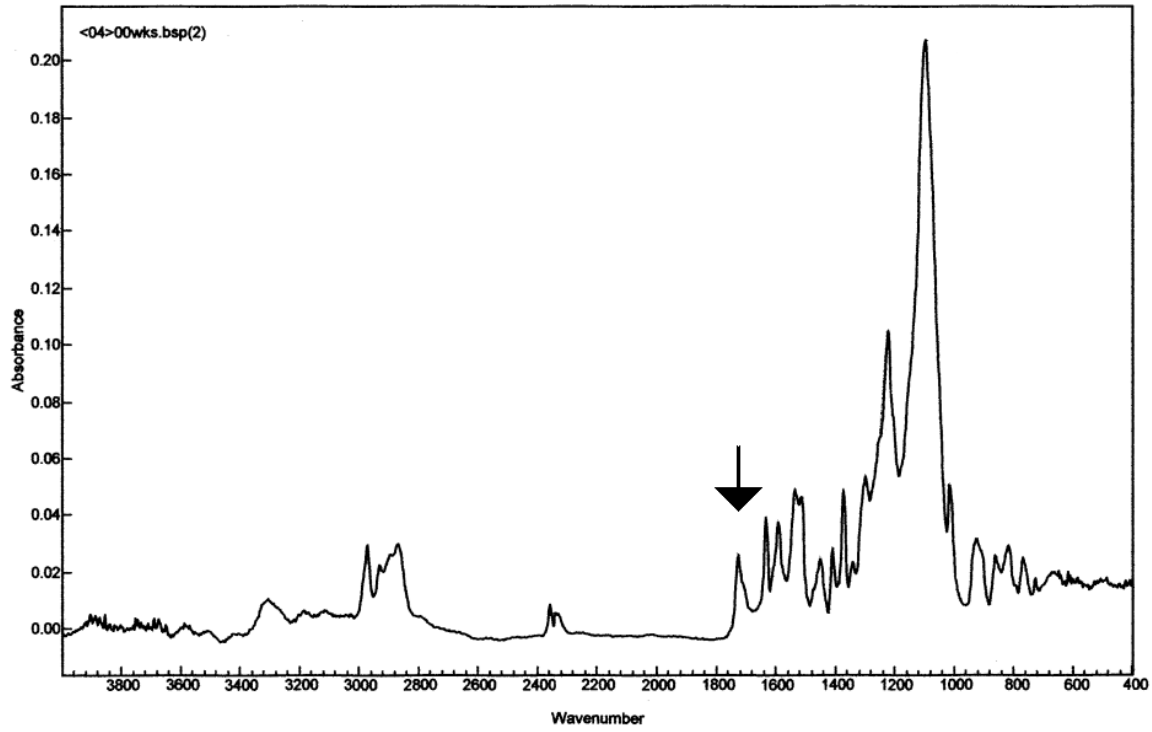


Figure 3.5.7. PPG based polymer, 50% fluorinated, unexposed.

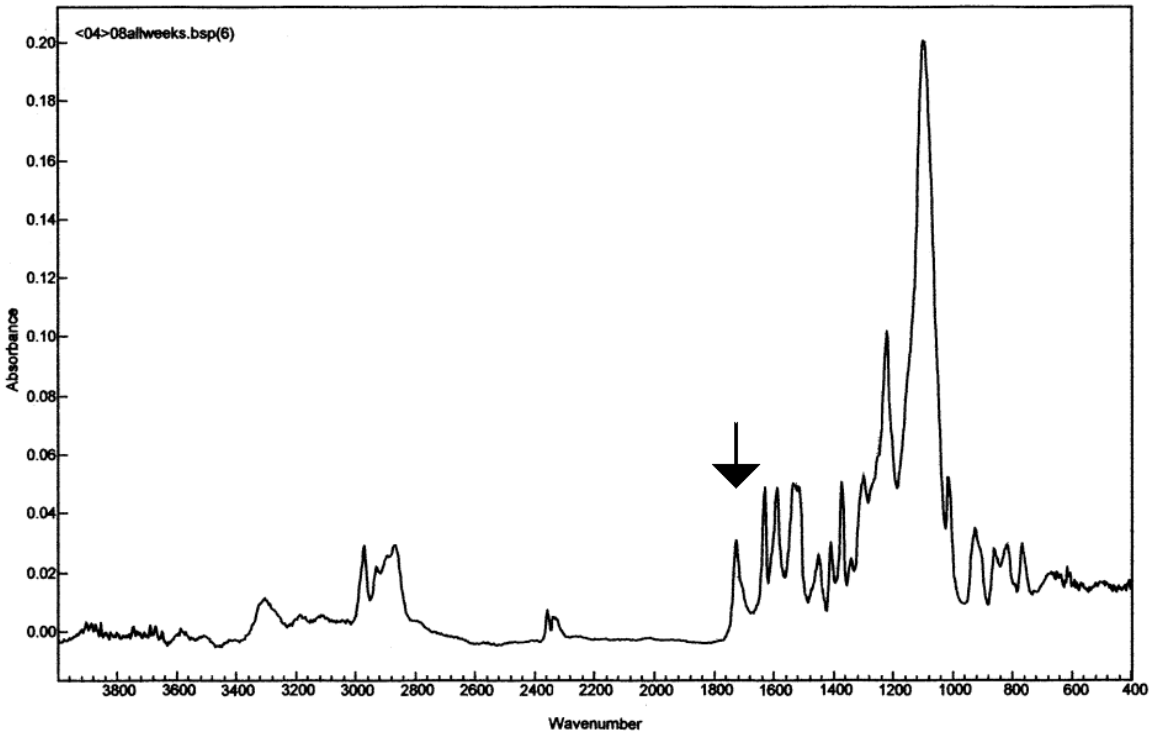


Figure 3.5.8. PPG based polymer, 50% fluorinated, exposed for 08 weeks.

3.6. Dynamic Mechanical Analysis

Tanδ results obtained from dynamic mechanical analysis of the non-fluorinated and 50% fluorinated PTMG and PPG samples are shown here according to their exposure times. Three-dimensional Tanδ curves were build for this section and were used for the analysis. Two-dimensional plots were then used, as composite plots, for the comparison and analysis of the effect of aging and the presence of fluorinated segments on the basic polyurethanes. Tanδ, storage modulus and loss modulus test results for all samples are shown on Appendix C. The Matlab® code designed for generating the surface plots for DMA is shown on Appendix D.

Results show that the presence of fluorinated segments on the unexposed PTMG based polyurethanes lower the main glass transition temperature of the polyurethanes (figure 3.6.1.). In addition, with the fluorinated groups a new peak in Tanδ around $-145^{o}C$ appeared, as shown on figure 3.6.2. The PPG based polyurethanes presented similar response to the PTMG based polyurethanes, with respect to the presence of fluorinated segments. In general, the glass transition temperature lowered with increasing fluorination (considering molecular weight differences of each sample, discussed in more details on section 4.6.) and a new peak was observed in Tanδ around $-145^{o}C$ (figures 3.6.3. and 3.6.4.).

The PTMG based PUs, when compared to the PPG based polyurethanes show significantly lower glass transition temperature. Another significant difference between the PTMG and PPG based samples is that the PPG based polyurethanes present a smooth curve for storage modulus for all frequencies, while the PTMG based polyurethanes present a multi-stage transition. The presence of fluorinated groups on the studied polyurethanes, lowers the storage modulus of the samples at temperatures below the glass transition and increased the modulus at temperatures above the glass transition of these materials.

Results show that the aging impacts negatively the dynamic behavior of these polyurethanes, as the storage modulus of the PPG based polyurethane decreases with exposure time. The PTMG based polymer, on the other hand, becomes stiffer with

exposure time, as the storage modulus increases with aging, but the changes in storage modulus along the exposure time become less significant as the percentage of fluorinated substitute segments increases, for both polyurethanes.

The results illustrated on the three dimensional figures 3.6.1. to 3.6.8. show the effect of aging on the Tanδ curves of the PTMG and PPG based polyurethanes studied. Note the Tanδ curves of the PTMG based polyurethane present a very unique shape after exposure, showing a peak at temperatures above the main glass transition, notable especially at higher frequencies. This new peak becomes stronger with aging and weaker with increasing degrees of fluorination. Figures 3.6.1., 3.6.2., 3.6.5. and 3.6.6. show the effect of aging on the Tanδ of PTMG based polyurethanes. Aging also raised the glass transition temperature of the PTMG based polyurethanes. For the PPG based polyurethanes, on the other hand, aging raised the glass transition temperatures only for the non-fluorinated and for the 10% fluorinated samples.

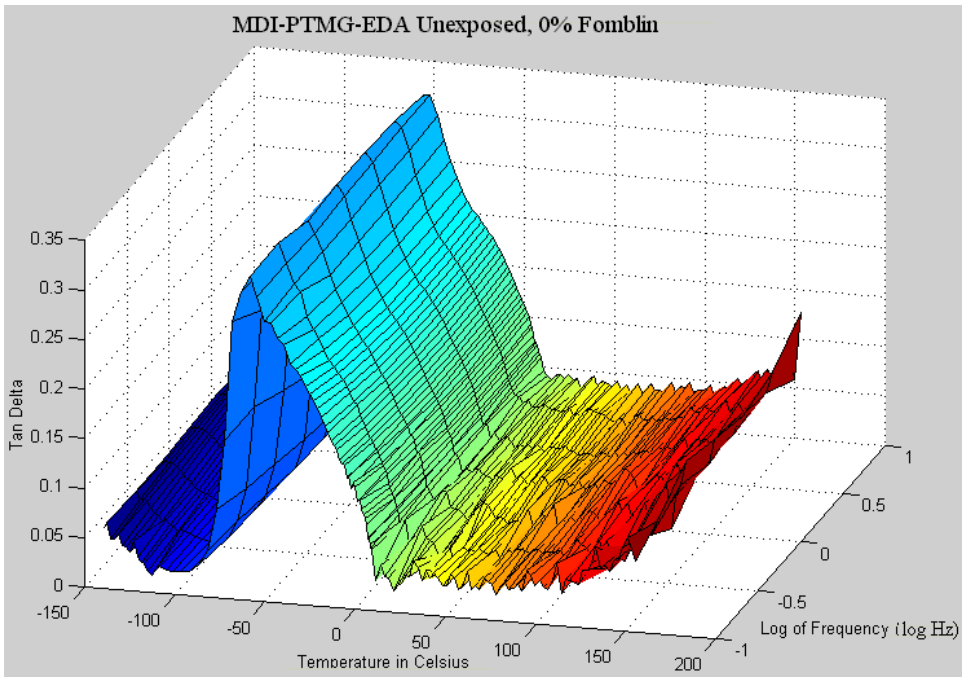


Figure 3.6.1. PTMG based PU, non-fluorinated, unexposed, Tanδ versus temperature.

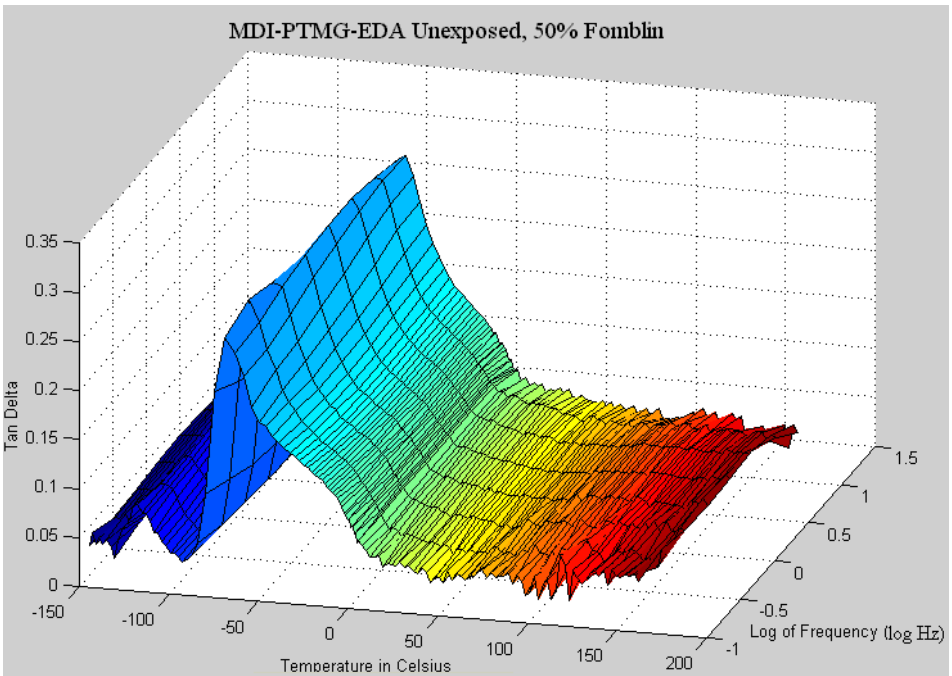


Figure 3.6.2. PTMG based PU, 50% fluorinated, unexposed, Tanδ versus temperature.

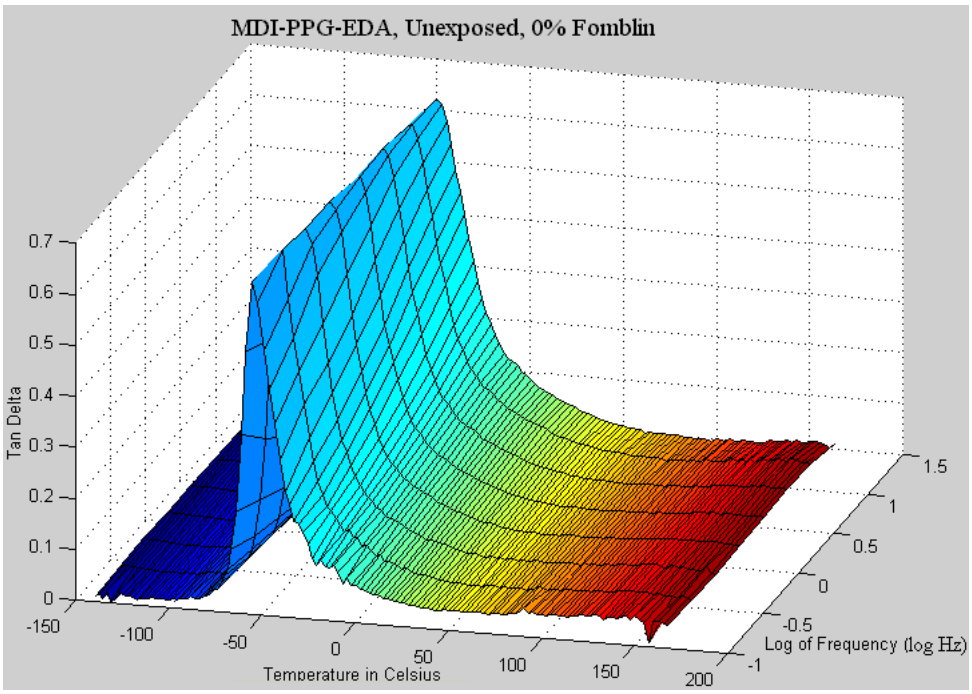


Figure 3.6.3. PPG based PU, non-fluorinated, unexposed, Tanδ versus temperature.

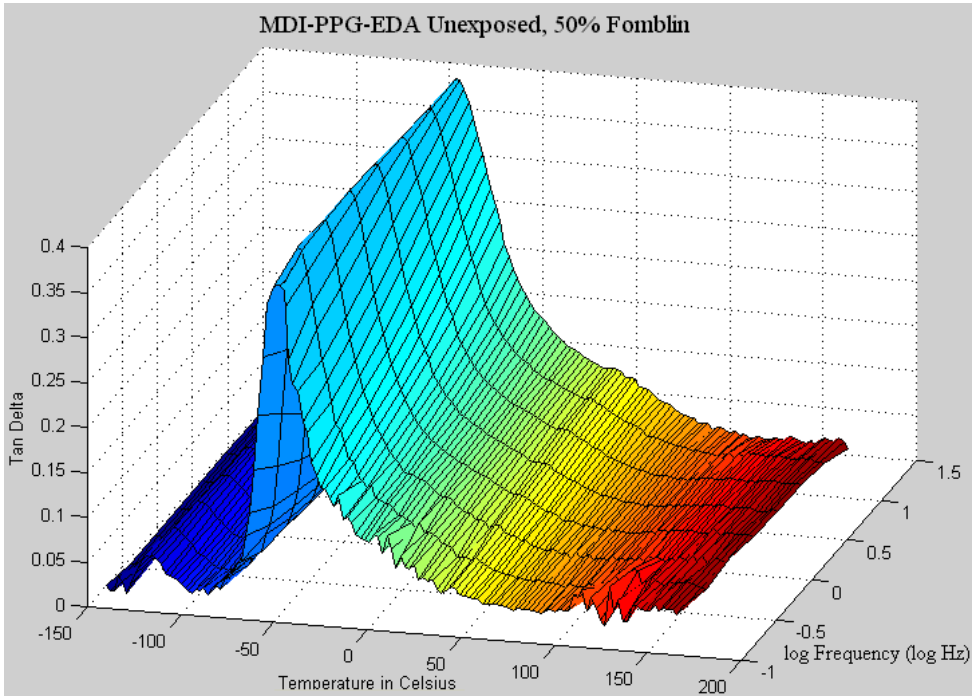


Figure 3.6.4. PPG based PU, 50% fluorinated, unexposed, Tanδ versus temperature.

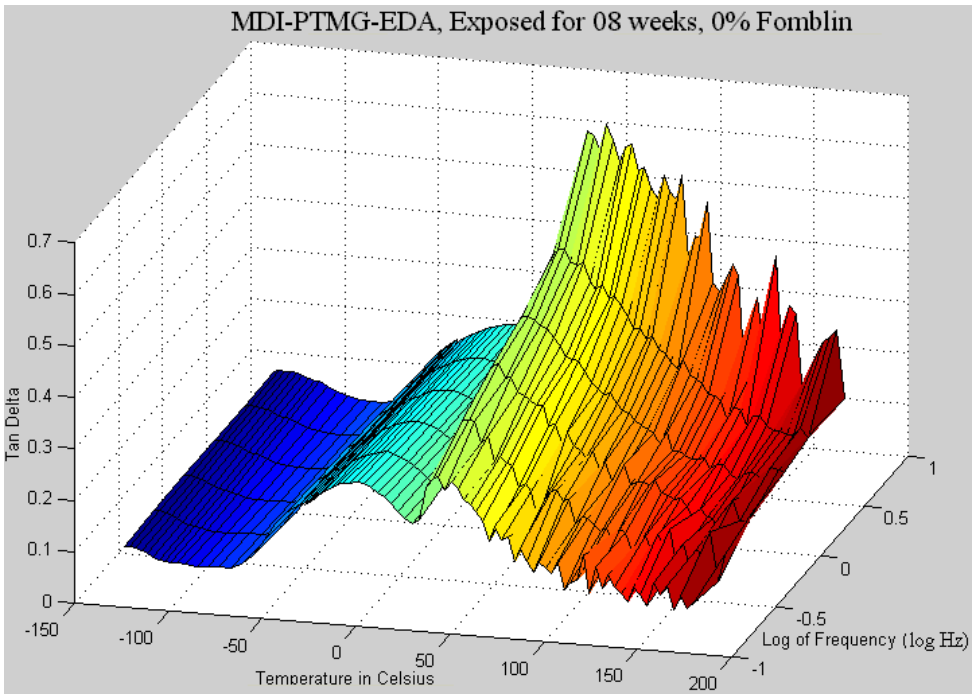


Figure 3.6.5. PTMG based PU, non-fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

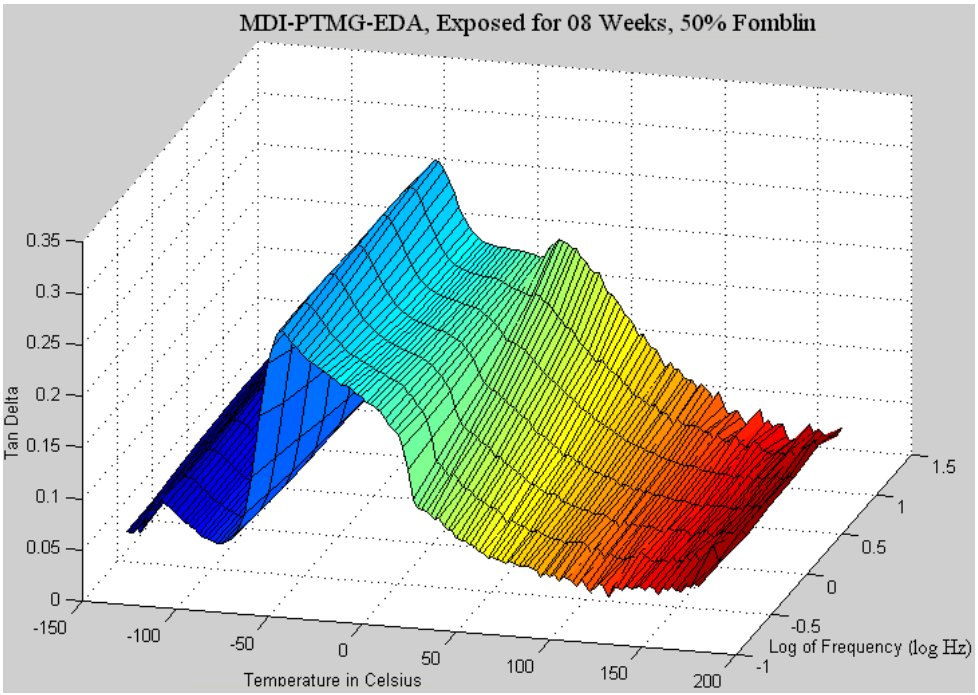


Figure 3.6.6. PTMG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

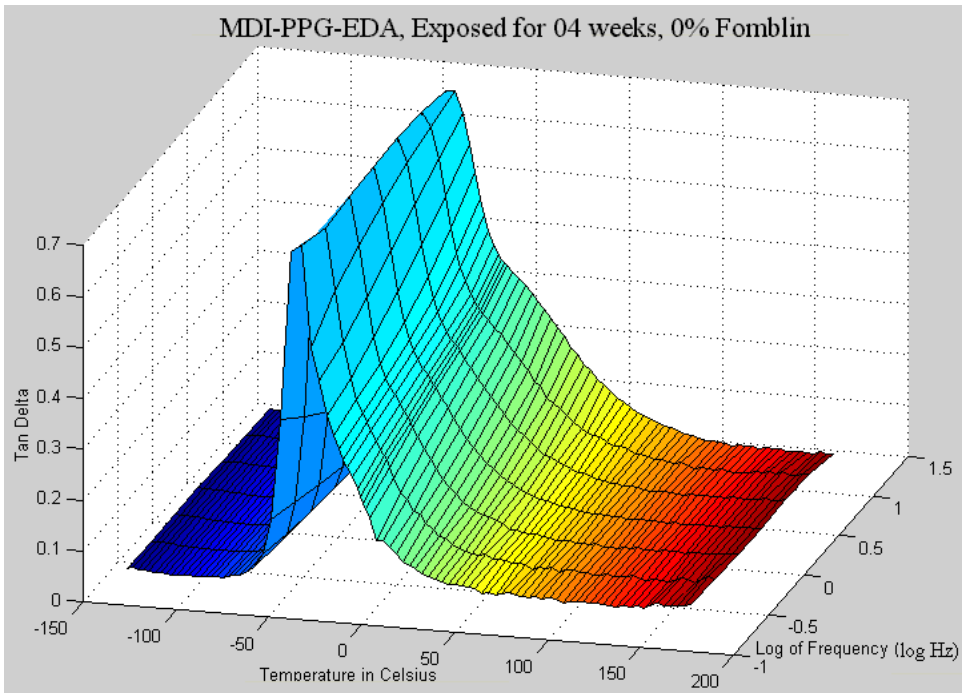


Figure 3.6.7. PPG based polymer, non-fluorinated, exposed for 04 weeks at 118±3°C, tanδ versus temperature.

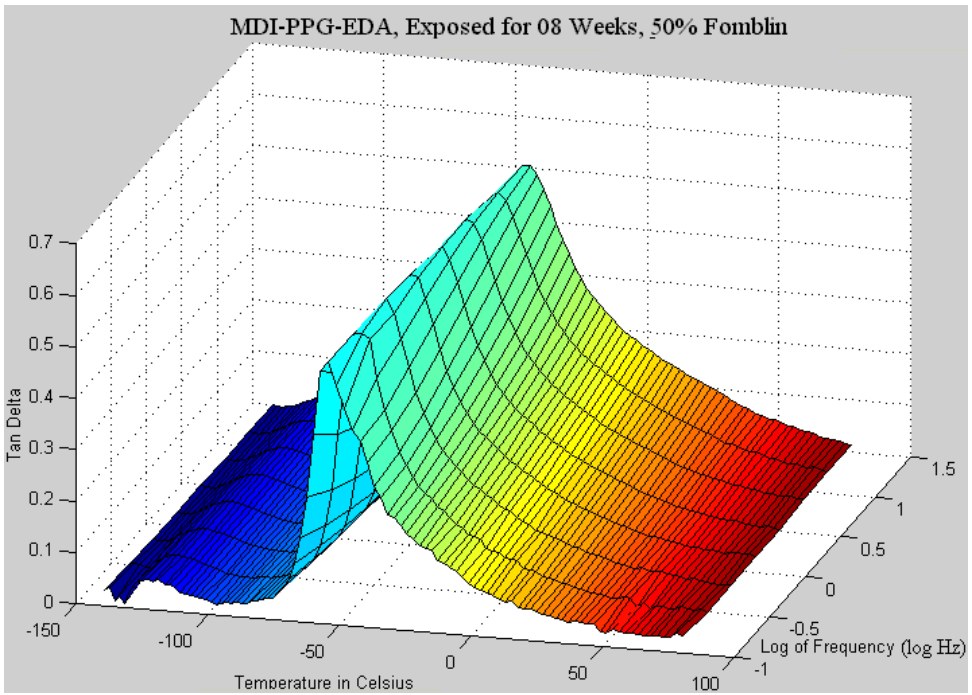


Figure 3.6.8. PPG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

4. Discussion

Since chemical reaction rates are accelerated at higher temperatures, one of the most common ways of forecasting the durability and consequences of aging in plastic materials is by exposing to a high temperature environment. The selected temperature should be high enough to promote significant changes on the tested materials with the designed exposure times. Polyurethanes in particular are well known for their yellowing during aging and like all other elastomers, loss of properties. This chapter will assess the results presented on chapter 3 and their correlation to the physical and chemical characteristics of the materials studied. Individual sections will be discuss the results obtained from each of the experimental methods. The discussions are presented in terms of type of soft segment (PTMG and PPG), degree of fluorination and exposure time.

4.1. Mass Loss

Oxidative degradation of polymers in general leads to the formation of peroxides and low molecular weight components and subsequent mass loss of the sample. The mass retention results are, as described in detail on section 3.1., a result of the average of (100 - %drop in mass) of each sample. The closer to 100% the value for mass retention, the less mass was lost due to the exposure. It is valid to mention that both fluorinated and non-fluorinated samples registered significant mass loss during the eight weeks of exposure at 118±3^{o}C. Greater mass loss was observed for the fluorinated polymers, as seen on figures 3.1.1. to 3.1.3.

Mass retention, in terms of thermal oxidation, is a function of the thermal stability of the samples or functional groups present in the polymer chain. PPG based PUs are more likely to suffer thermal-oxidation when compared to PTMG based PUs due to the presence of the reactive tertiary carbon on the former. The better thermal stability of the PTMG based PU promoted a small but significant lower mass retention of this material when compared to the PPG based polyurethane tested, as shown in figure 4.1.1. The difference between the PTMG and PPG based PUs, although not large, is consistent.

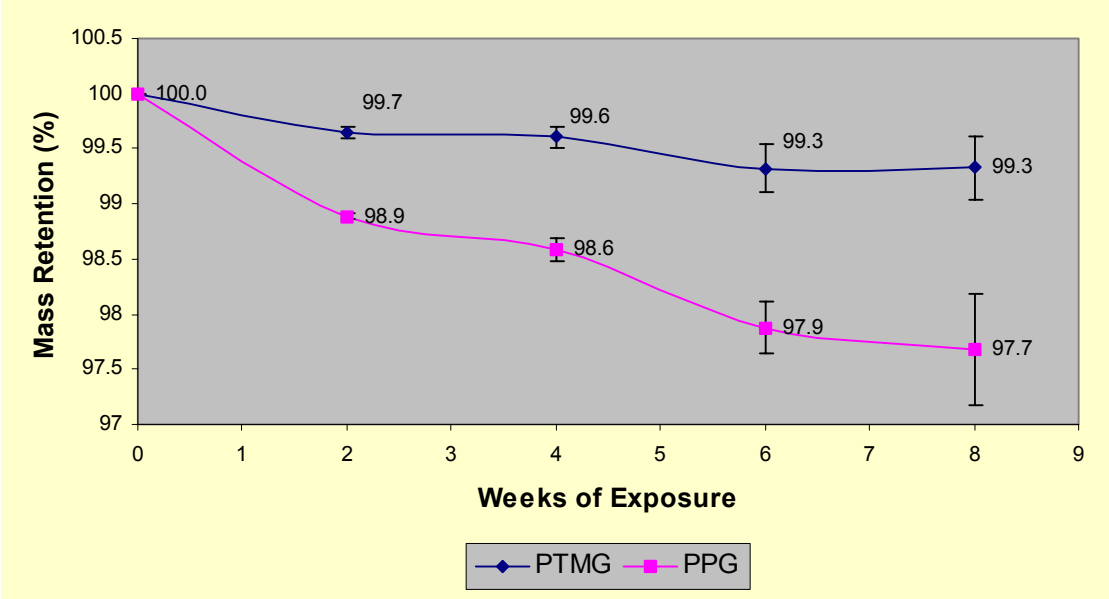


Figure 4.1.1. Mass retention of non-fluorinated polymers.

From 0.8% change for 02 weeks to 1.6% change for the 08 weeks, the values are within a maximum of ±0.75% difference (08 weeks). The increasing error most visible on figure 4.1.1.) with exposure times is due to thickness variation on the initial samples, a function of oxygen diffusion. The error will be zero for the unexposed samples and as each sample was purposely chosen from different areas of the cast film, they will have slightly different weight loss characteristics.

Perfluorinated groups are known for their good thermal stability (refer to section 1.2. for more details) and ability to improve the thermal tolerance of polymers. For polyurethanes, on the other hand, the presence of fluorinated groups enhanced the overall mass loss of the samples with aging, as shown on figures 4.1.2. and 4.1.3. Assuming that for PUs mass loss in isothermal degradation is associated with changes in the hard segments [4,37], the new environment the hard domains are found with the shorter fluorinated chains lead to an acceleration of the process. The shorter fluorinated segments will cause more of the hard segments to be dispersed in the soft matrix, changing the dynamics of the degradation mechanism. The soft segments overall lengths according to the degree of fluorination will be discussed in details on section 4.2.

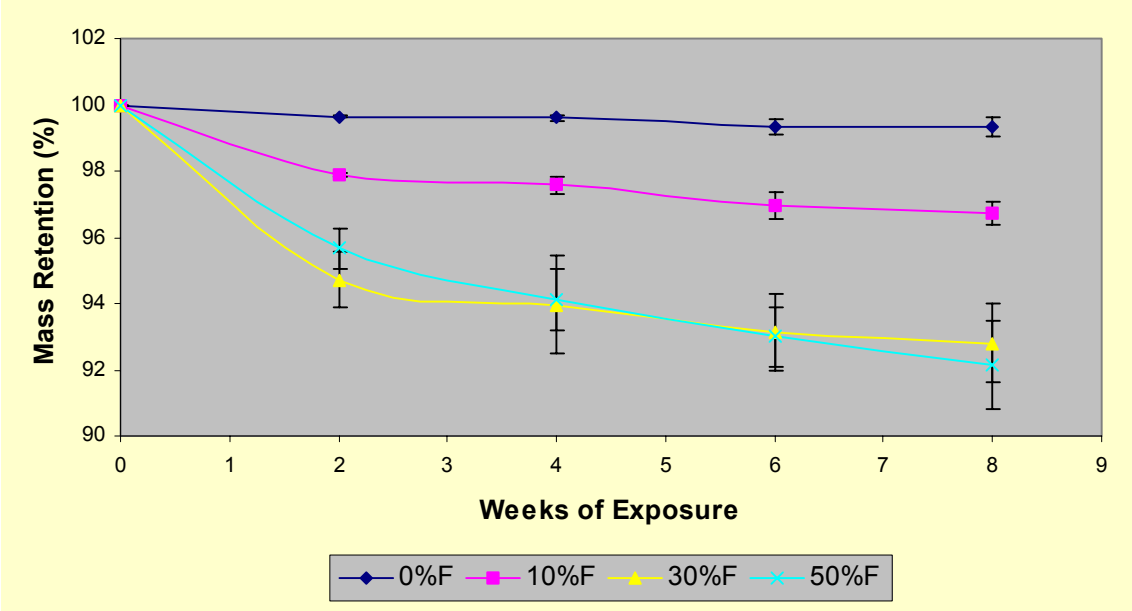


Figure 4.1.2. Mass retention of PTMG based polymers.

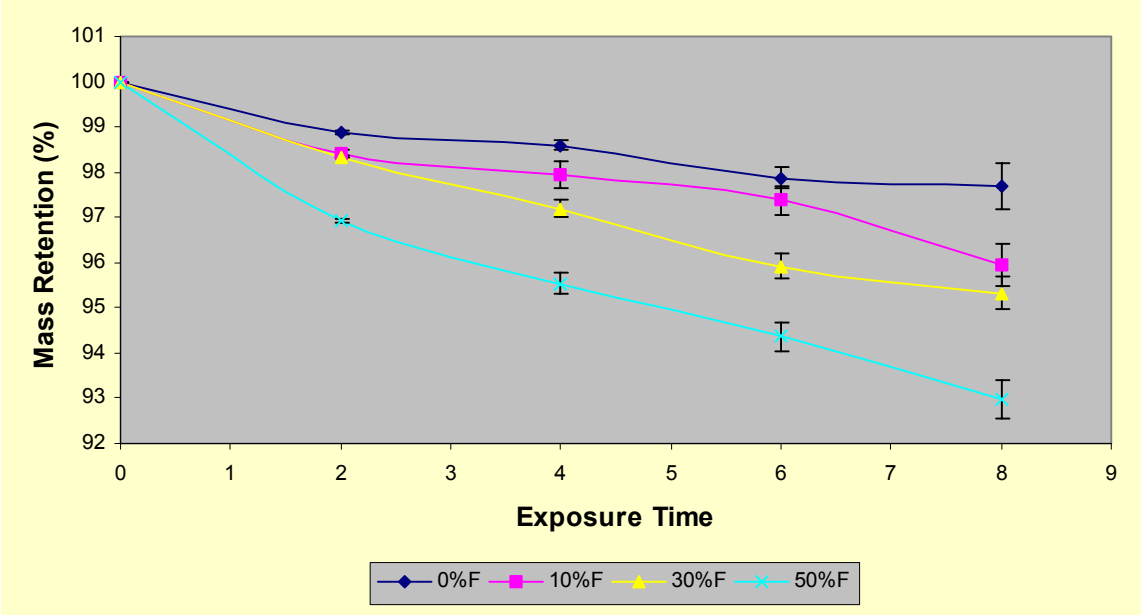


Figure 4.1.3. Mass retention of PPG based polyurethanes.

4.2. Surface Wettability

Lower surface tension liquids will generate enhanced wettability, a desirable property of glues. For solids, on the other hand, lower surface tensions will generally produce poor surface wettability. An ideal hydrophobic polymer will have very low surface tensions and will cause a liquid of high surface tension to bead on its surface, as in the case of water beading in PTFE. [38]

The difference in contact angles on solids surfaces can be rationalized simply. Water has a relatively high surface tension (73mN/m) and its surface tension (intermolecular forces) has a substantial contribution from hydrogen bonding forces. The surface tension of highly electronegative materials (e.g. fluorinated polymers) results in almost entirely dispersive forces, making it almost impossible for interactions between fluorinated surfaces and water. [38]

In fact, water is a very special solvent for the study of contact angles. Highly hydrophobic polymers will generate contact angles in water bubbles in excess of 100^{o}. Low contact angles in tests with water is due to the great number of hydrogens that have the tendency to bond to neighboring atoms. [23] It promptly does so if the conditions are favorable for bonding, spreading the water bubble. If the conditions are not favorable, on the other hand, water will have the natural tendency to form bubbles, large in size when compared to most solvents. [23]

At the same time PTFE illustrates the influence of fluorination of PE on its wettability, analogous response would be expected when FPUEs, as the active element here is fluorine (very electronegative element). The main difference is certainly due to the fact that not all groups in PUs will be fluorinated as in the case of PTFE. With respect to the materials used on this work, at most 50% of the soft segments (only) were perfluorinated. In addition, not all atoms in the main chain of the fluorinated segment contain fluorine, as opposed to PTFE. The result is that the increase in contact angles observed in the polyethylene to PTFE systems could be partially observed in polyurethanes, due to the non-fluorinated segments in the polyurethane chain. In fact, the

contact angles increased as much as 15% for the PTMG based samples for the 50% fluorinated sample, as illustrated on figure 3.2.1. This enhancement can be of extreme importance for some applications such as carpeting and surface coatings, but is not near the gain observed in PE/PTFE.

The presence of fluorinated soft segments is inarguably favorable to promoting poor surface wettability due to its water repellant characteristics, but the increase in contact angle is not a linear function to the degree of fluorination. The contact angle is a direct function of the hydrophobic groups on the surface of the materials. As an example, the contact angle values for the PPG based polyurethanes tend to level off after a certain percent degree of fluorination, as illustrated on figure 4.2.1. The leveling of contact angle measurements of a similar PTMG based polyurethane was observed by Kim [11] to occur above 50% fluorination. The number of atoms per repeat unit of the polyurethane chain is of great importance in the resulting surface tension of the studied polyurethanes. For Fomblin Z-dol 2000® (soft segment substitute), the heaviest atoms (F) are not part of the main chain, and there will be only around 56 atoms on each fluorinated soft segment separating MDI groups (hydrophilic), estimating ‘m’ and ‘n’ in the chemical structure (figure 2.1.3.) to be 11 and 8, respectively. PTMG and PPG based polyurethanes, on the other hand, will have much longer chains (135 and 102 atoms, respectively), that means the MDI units of the fluorinated polyurethane will be much closer when compared to MDI units of the non-fluorinated PU (table 4.2.1.). The number of atoms (distance) between each MDI unit will affect the frequency of which MDI will occur per unit length. This relationship is illustrated on figure 4.2.2. where the MDI segments will be closer to each other for the shorter soft segment polymers.

The PPG based PUs presented better wettability than the PTMG based PUs, as shown on figure 4.2.1. The length of the soft segment is therefore important to the surface wettability of the polyurethanes studied. With respect to the degree of

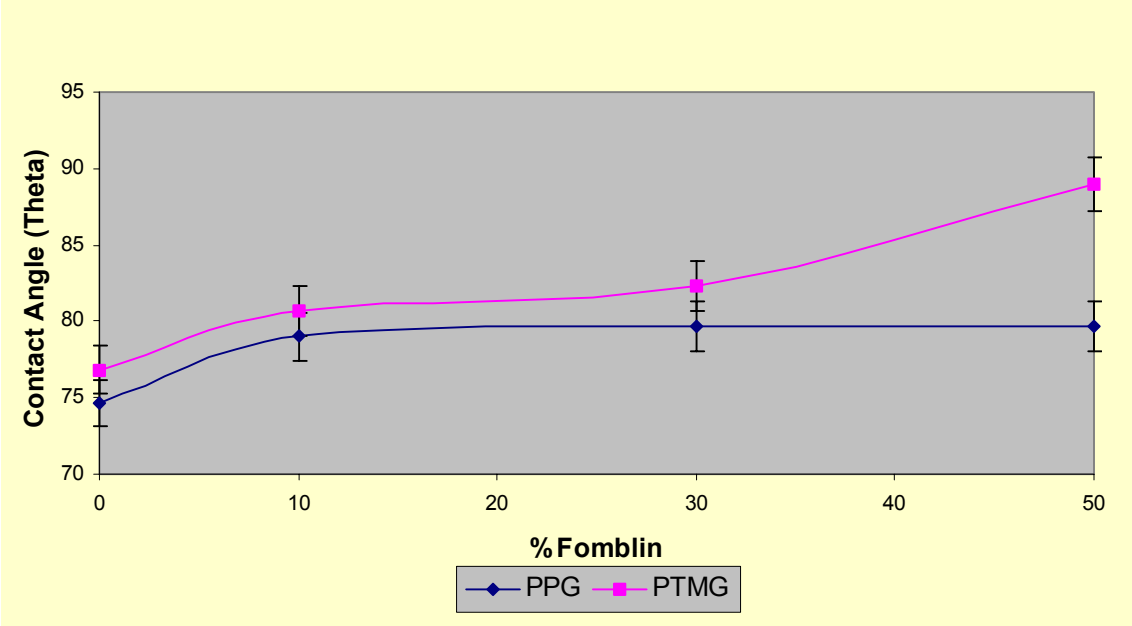


Figure 4.2.1. Contact angle for unexposed samples versus percentage of fluorinated soft segment.

Table 4.2.1. Estimated average number of atoms between the MDI segments on the ends of the soft segments.

	PTMG	PPG
+0% Fomblin	135	102
+10% Fomblin	127.1	97.4
+30% Fomblin	111.3	88.2
+50% Fomblin	95.5	79
Δ	~ 40	23

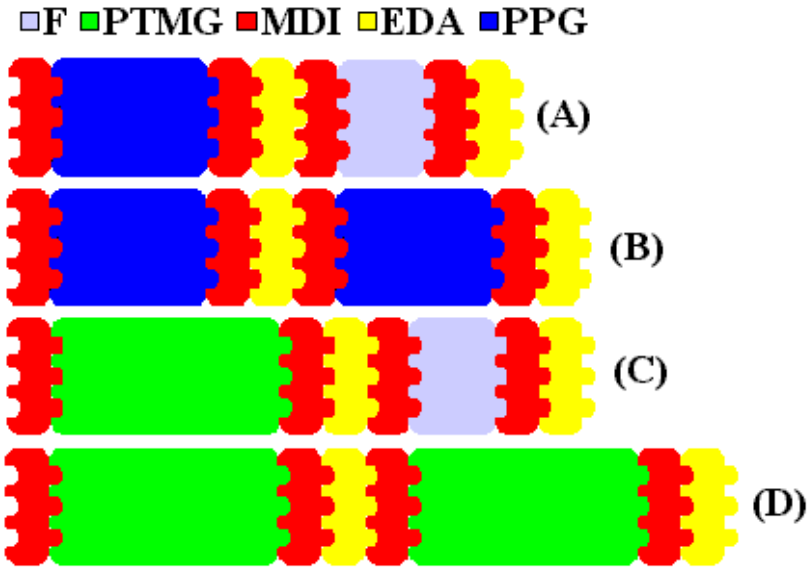


Figure 4.2.2. Diagram of some of the studied polymers structures with respect to segments lengths. (A) PPG polymer with 50% fluorinated soft segment, (B) PPG polymer with 0% fluorinated soft segment, (C) PTMG polymer with 50% fluorinated soft segment, (D) PTMG polymer with 0% fluorinated soft segment.

fluorination, a different approach was used. Although the medium chain length of the soft segment is reduced with the increase in degree of fluorination, surface tension is reduced with the presence of fluorinated segments due to the high water repellant characteristics of fluorine.

Aging on the PPG based PUs caused chain scission and therefore increasing chain mobility which allows the hard (MDI) domains increase in size, reducing the domains overall surface area. The reduced surface area minimizes the hydrophilic effect of the benzene rings present in MDI, raising the contact angle of the material. The results of the contact angle and mass loss of the studied PPG based material is shown on figure 4.2.3. Note the general tendency for the contact angle to increase with the mass loss, as in the first week and last four weeks. On figure 4.2.3. 'RR' represents 100 times the reciprocal of the polymer mass retention (100/mass retention in percent).

In the case of the non-fluorinated PTMG based PU, the correlation observed for the PPG PU does not work, mainly due to the insignificant changes in the mass loss and

due to crosslinking and increase in hydrogen bonded carbonyl density of PTMG with aging (more on chemical structure changes in section 4.5.). Figure 4.2.4. shows the small changes in mass loss and the non-dependence of the two variables for PTMG based PUs.

Chain mobility and molecular weight are closely related. In the case of the PPG based PUs, aging causes reduction in viscosity (section 4.3.) and mass (section 4.1.). The more mobile MDI segments will consequently aggregate groups with more ease, reducing the surface area of the MDI domains (evidenced by the decrease in Tg of PPG based Pus, discussed on section 4.6.). The dependence of chain mobility with the contact angle shows that for segmented MDI based PUs, the surface tension (thus wettability) is expected to influence the size of the MDI domains and its surface area. The smaller the MDI domains will be, the bigger the surface area and therefore the overall polymer will become more hydrophilic. For the PTMG segments, on the other hand, aging promotes crosslinking along with an increase in hydrogen bonded carbonyl groups density, inhibiting changes in the size of the MDI domains. A proof that chain scission occurs in the PPG based PU is the gain in chain mobility with aging, as a reduction in the Tg of these polymers was observed. (more details on section 4.6.)

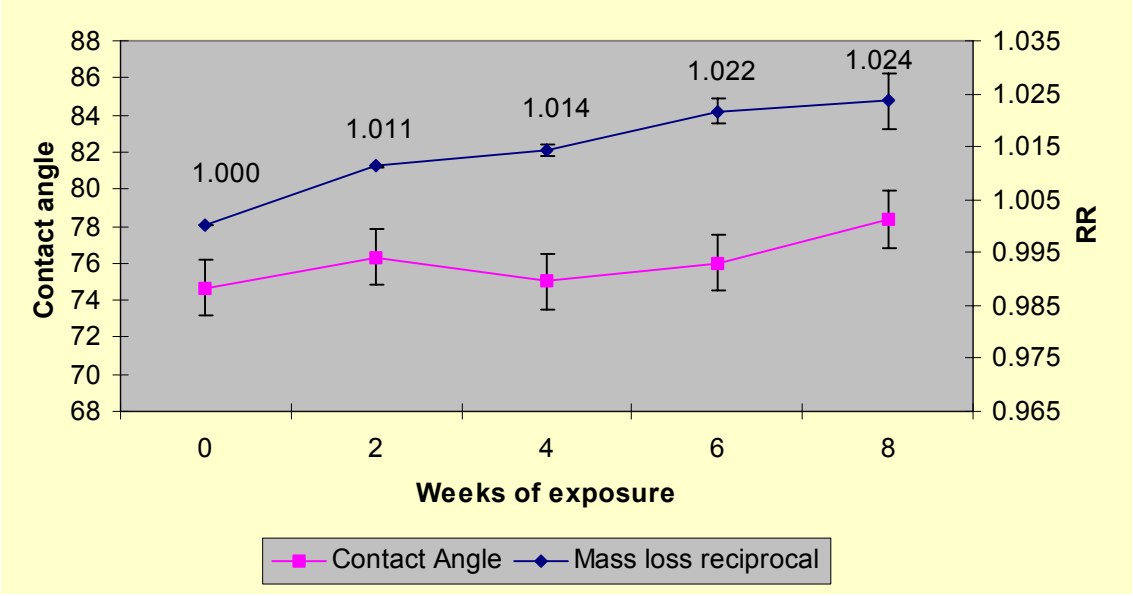


Figure 4.2.3. Contact angle and reciprocal of mass retention (RR) for the PPG based non-fluorinated polyurethane.

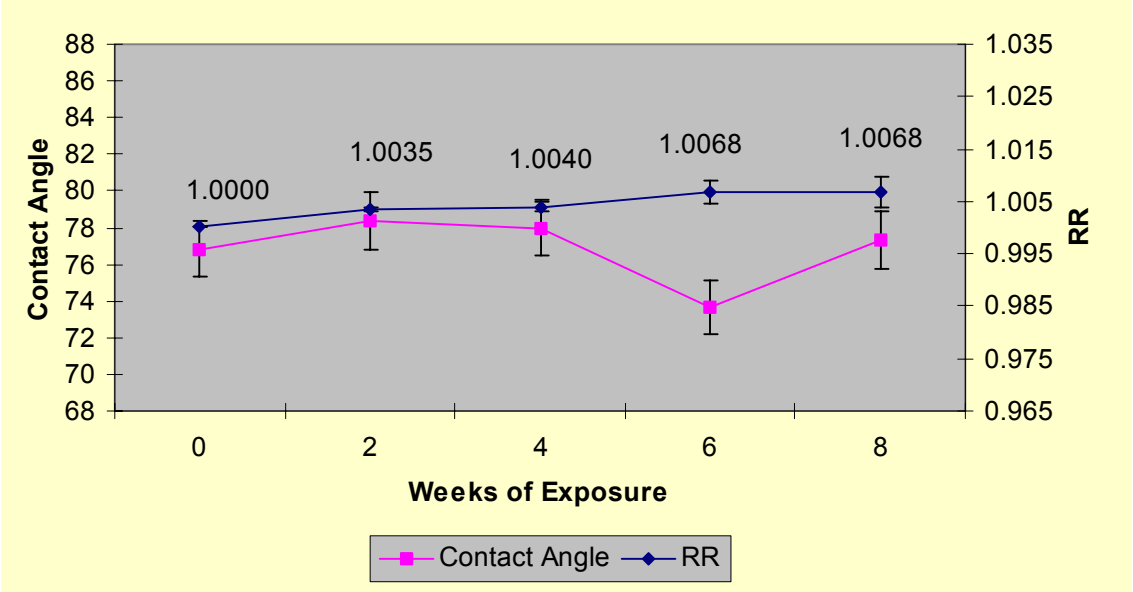


Figure 4.2.4. Contact angle and reciprocal of mass retention of non-fluorinated PTMG based PU along exposure time.

Figures 4.2.1. and 4.2.5. to 4.2.8. compare the contact angles of PTMG and PPG based polyurethanes according to degree of fluorination. Note that for the unexposed samples (figure 4.2.1.) the PPG based polyurethanes presented lower values for contact angles in comparison to the PTMG based materials, especially for the 50% fluorinated samples. With exposure time, the PPG based polyurethanes became more hydrophobic while the PTMG based materials presented more stable values for contact angles with respect to aging. The contact angle stability of the PTMG based polyurethanes with aging is attributed to the soft segment crosslinking (discussed on section 4.3.) and increase in hydrogen bonded carbonyl density (discussed on section 4.5.). Crosslinking reduces chain mobility, inhibiting changes in the surface area of MDI domains, and hydrogen bonding the newly generated carbonyl (due to thermal oxidation, discussed on section 4.5.) will eliminate the hydrophobic effect of the carbonyl oxygen atom. The fact that aged PTMG polyurethanes did not dissolve (section 4.3.) and the glass temperature increased for these polymers, illustrating a reduction in chain mobility of the studied PTMG based polyurethanes.

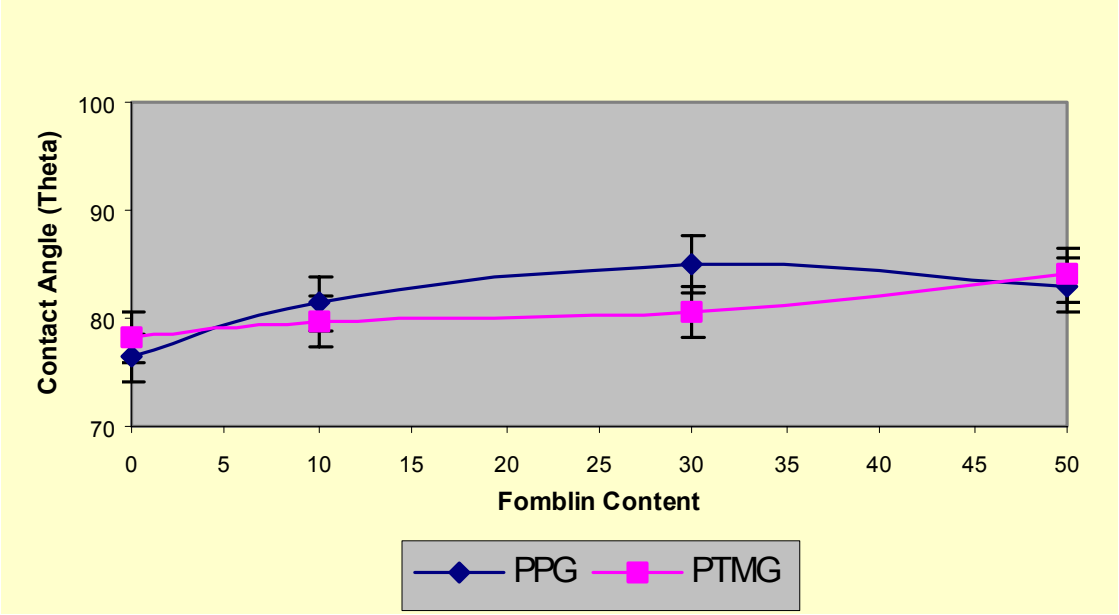


Figure 4.2.5. Contact angle for 02 weeks samples versus % fluorinated soft segment.

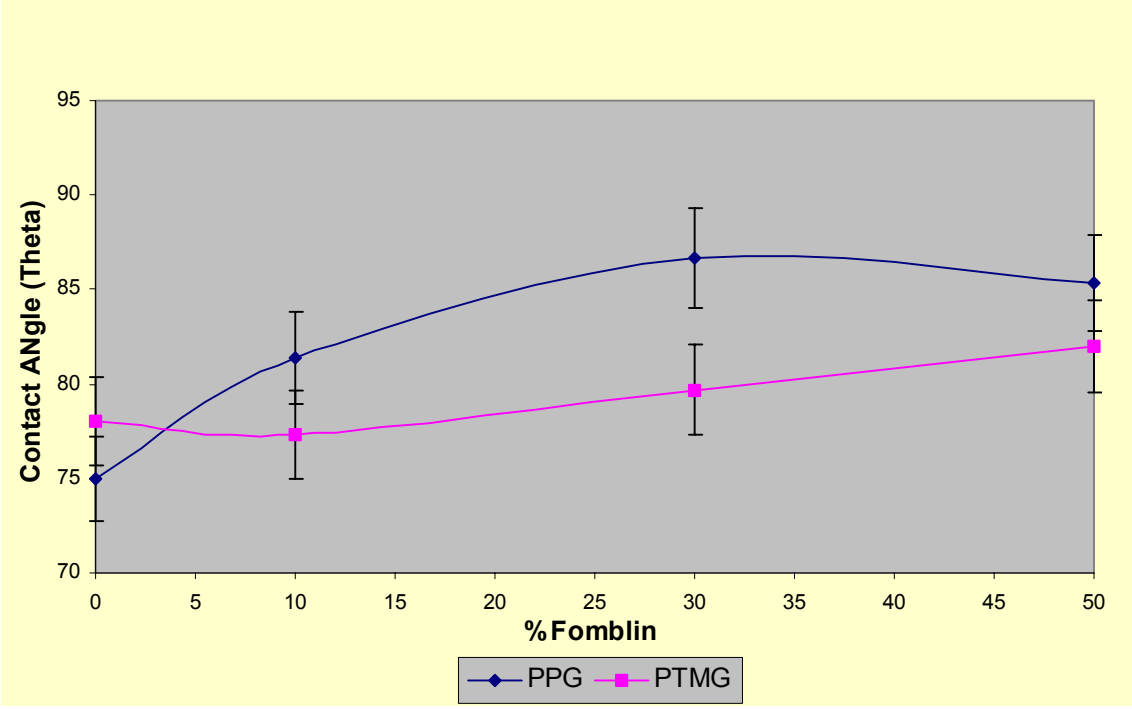


Figure 4.2.6. Contact angle for 04 weeks samples versus % fluorinated soft segment.

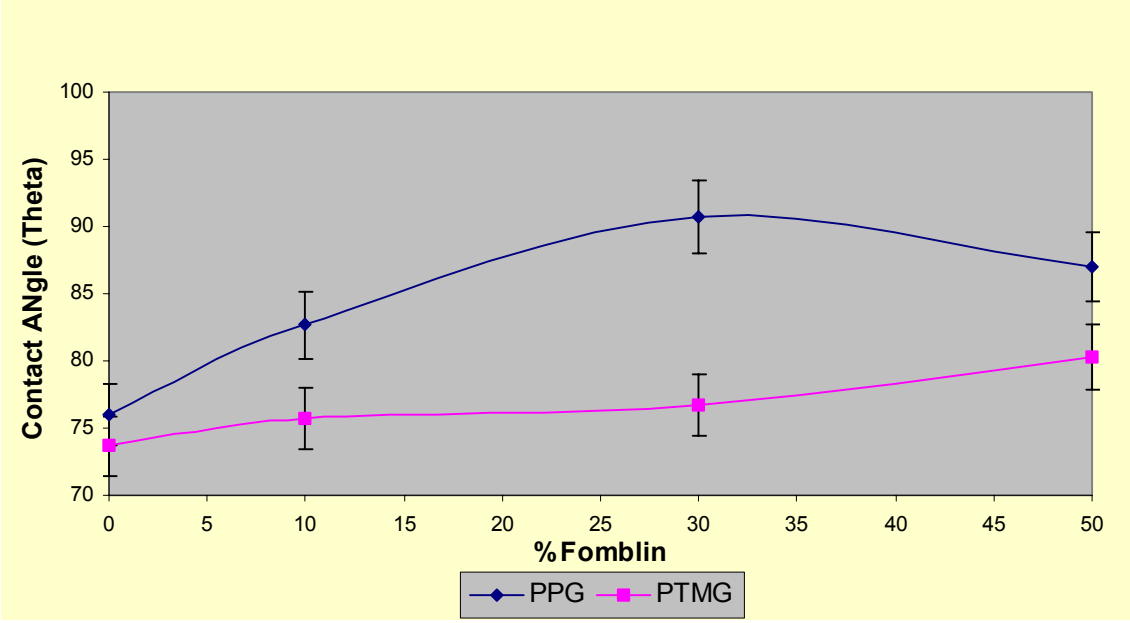


Figure 4.2.7. Contact angle for 06 weeks samples versus % fluorinated soft segment.

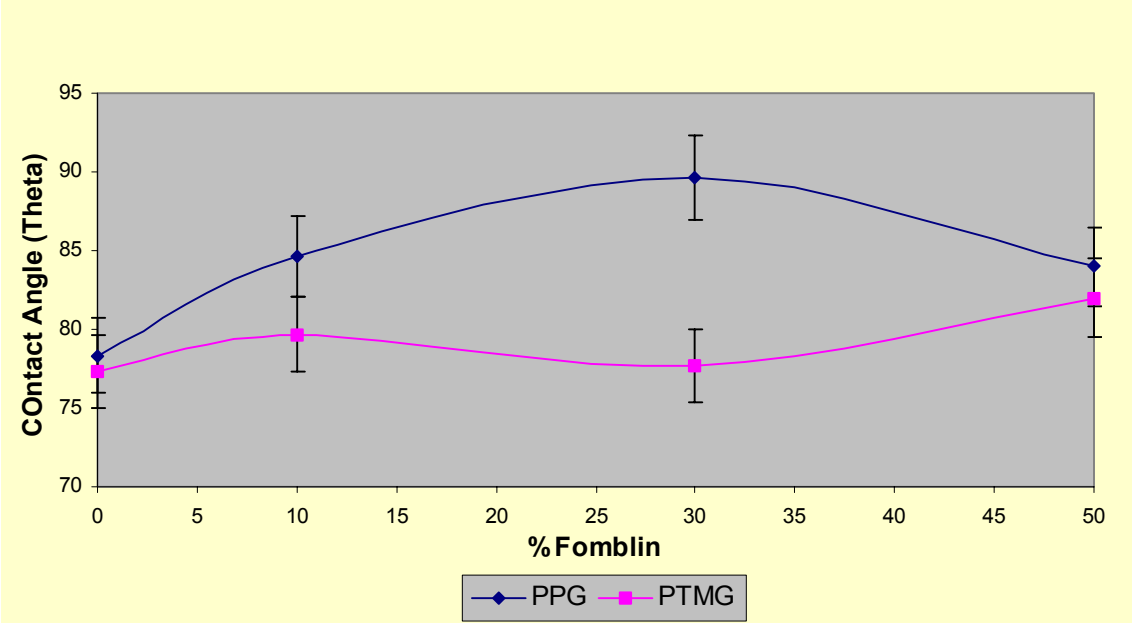


Figure 4.2.8. Contact angle for 08 weeks samples versus % fluorinated soft segment.

4.3. Intrinsic Viscosity

For a given molecular weight, intrinsic viscosity is a function of chain architecture. PTMG is a linear glycol, and for that reason the PTMG chain is longer than the PPG, offering more contact points in solution, slowing down the solution flow. In segmented polyurethanes, the average chain length of the soft segment is reduced with increasing degree of fluorination, making the solution more fluid. As the molecular weight of the fluorinated soft segments are similar to the molecular weight of the PPG and PTMG, the fluorinated polyurethanes will have an overall shorter chain as the latter has heavy fluorine atoms in place of hydrogens of the former two, as discussed on section 4.2. The significantly shorter (yet linear) fluorinated chains allow more movement of the diluted chains as suggested by the PTMG based polymers, illustrated on figure 3.3.1. in the previous section. Figure 4.3.1. shows a decay in viscosity for the PTMG based polyurethanes, especially for the 30 and 50% fluorinated samples. The 10% fluorinated polyurethane showed a slight decrease in viscosity when compared to the non-fluorinated polyurethane.

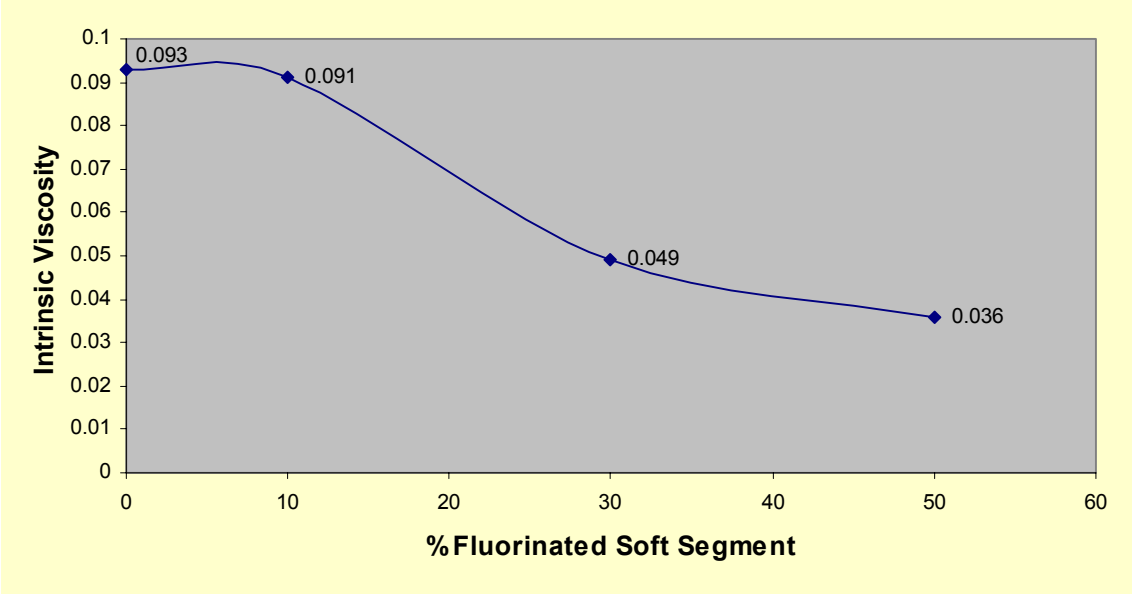


Figure 4.3.1. Calculated intrinsic viscosity of unexposed PTMG based samples as a function of degree of fluorination of soft segments.

The 10% fluorinated PPG based polyurethane resulted in the highest viscosity value among all degrees of fluorination, as illustrated by figure 4.3.2. The 10% fluorinated polymer, specifically is the highest molecular weight polymer of the PPG based materials tested (table 2.1.2.). The higher molecular weight certainly accounted for the higher value in intrinsic viscosity. In addition to the molecular weight, chain length and flexibility weight the overall chain hydrodynamics. The smaller number of atoms on the fluorinated segment will make the overall chain smaller lowering the polymer viscosity, as observed for the 50% fluorinated PPG based polyurethane (as show on figure 4.3.2.).

The presence of fluorinated groups helped maintain the viscosity during exposure for the PPG based polyurethanes, although mass loss results show increasing degradation for the fluorinated polymers. The maintenance of viscosity could be the effect of network formation and a competing effect of this network with the breakdown of the polymer chain along the exposure times, justifying the maintenance of the viscosity of the 50% fluorinated polymer (figure 4.3.2.). When comparing the intrinsic viscosity values

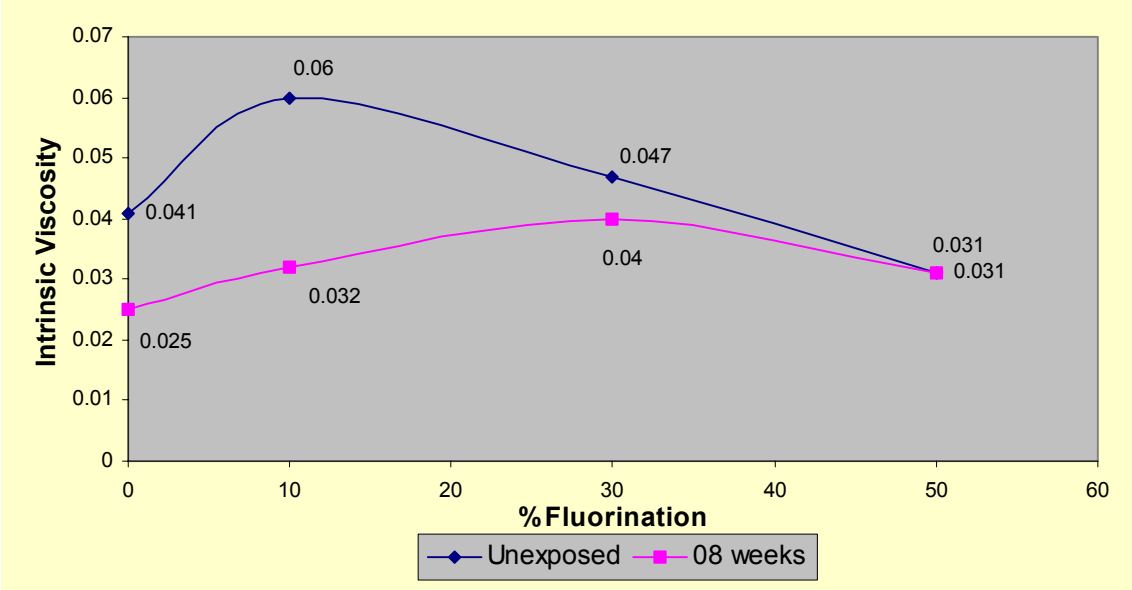


Figure 4.3.2. Intrinsic viscosity for the PPG based samples before and after exposure.

for unexposed PPG and PTMG based polyurethanes (figures 4.3.1. and 4.3.2.), it is suggested that the longer PTMG chains will be more effective than the shorter PPG chains in terms of slowing down the flowing process in solution.

The presence of fluorinated groups accelerated the process of mass loss in PUs , while the viscosities of the exposed samples were maintained more efficiently with increasing fluorination. The reasons for such contrasting behavior is still unknown but this is an indication that mass losses and viscosity drops are correlated with different segments of the materials, for instance being the mass loss due to changes in the hard segment and viscosity drop due to changes in the soft segments.

The PTMG based PUs did not dissolve after thermal exposure, a typical characteristic of crosslinked polymers. In addition to crosslinking, an increase in the density of hydrogen bonded carbonyl groups was observed for the PTMG based PUs, making the dissolution of the sample difficult. The increase in hydrogen bonded carbonyl groups was identified by infrared characterization (section 4.5.). Figure 4.3.3. contains the results for the unexposed PPG based PU for increasing fluorination. Note the 50% fluorinated polymer maintained its viscosity with exposure.

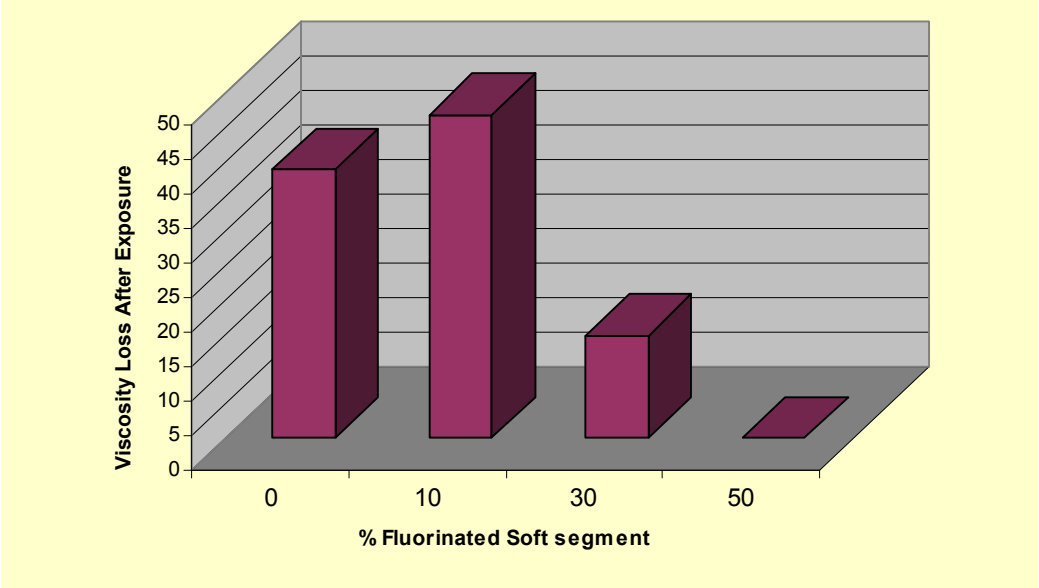


Figure 4.3.3. Chart of the intrinsic viscosity loss after 08 weeks of exposure for the PPG based polymers as a function of the degree of fluorinated soft segments.

4.4. Thermal gravimetric analysis

TGA results show the soft segment play an important role on the onset of degradation of polyurethanes. While the onset of degradation of both PTMG and PPG based polyurethanes are very similar, the end of reaction temperature (degradation end temperature) is much higher for the PTMG based polyurethane when compared to the PPG based polyurethane (368°C vs 438°C). The initial mass loss on the TGA curves of all studied polyurethanes is attributed to the loss of the hard domains, due to the fact that the degradation of the urethane and urea linkages are the first major changes in the chemistry during TGA analysis (160-200°C). The subsequent mass loss is attributed to the degradation of the polyglycols. PTMG is more thermally stable than PPG [3,4], because the low activation energy of the α-carbon on the backbone of the latter will promote rapid degradation of the polyglycol. In addition, the degradation temperature of PPG and the hard domains are relatively close, generating a smoother mass loss curve when compared to the PTMG based polyurethane. The onset of degradation and end of reaction temperatures are summarized on table 3.4.1. while the curves of the non-fluorinated, unexposed PTMG and PPG based polyurethanes are shown on figure 4.4.1.

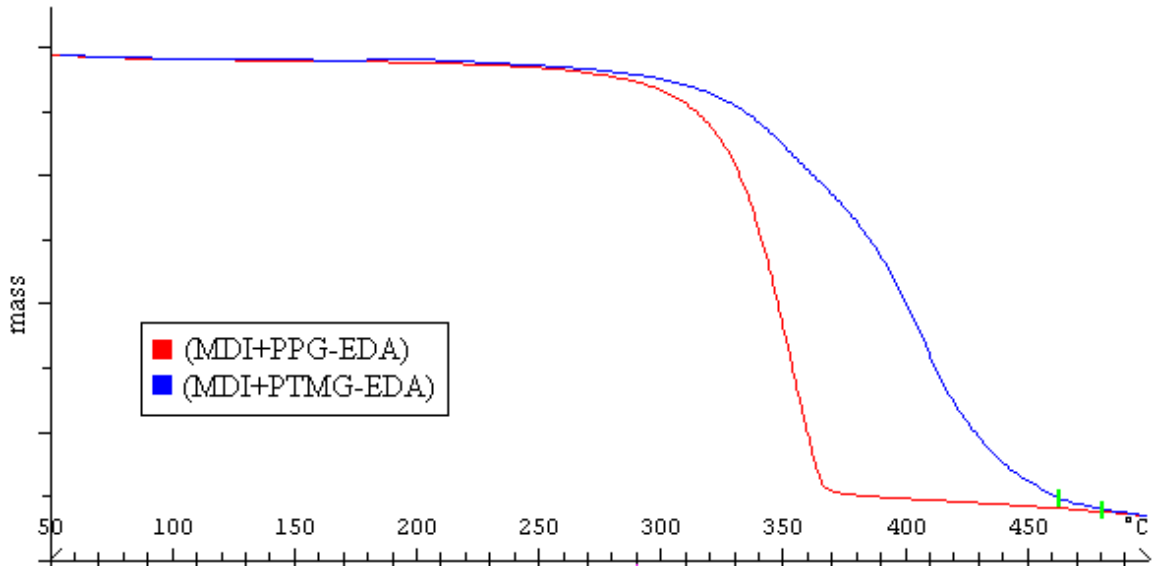


Figure 4.4.1. TGA curves for the non-fluorinated PPG and PTMG polymers.

TGA curves show a significant difference between the non-fluorinated and the fluorinated polyurethanes (figures 4.4.2. and 4.4.3.). For increasing fluorination, there is a substantial reduction in the onset of degradation of the hard domains, for both PTMG and PPG based polyurethanes. It was previously suggested that the length of the soft segment is very important for the temperature at which the mass loss will begin in thermal gravimetric tests. [14,15, 5] It was also suggested that in such complex systems as segmented polyurethanes, the thermal stability is governed not necessarily by the weakest link, but by the most frequently occurring one and chemical environment of the given group. [14] The building block diagram illustrated on figure 4.2.2. shows the importance of chain length in the overall polymer architecture. Although there is not a clear explanation of why the onset of degradation of the hard segments is reduced with increasing fluorination, this process is likely associated with a different environment of the hard domains for increasing fluorination, caused by the reduction of the soft segments average length. The shorter soft segments will promote increasing restrictions in phase separation similarly to lower molecular weight polyglycols polyurethanes. [16]

The end of reaction temperature for increasing fluorination promoted different results for the different base soft segments polyurethanes. While for the PTMG based polyurethanes there was not a significant change in the end of reaction temperature, for the PPG based polyurethanes a shift to higher temperatures was observed. The shift to higher temperatures in the PPG based PU is attributed to the better thermal stability of the fluorinated segments that will only degrade at a higher temperature than the non-fluorinated polyol. In the case of the PTMG based PUs, the end of reaction temperature of the fluorinated polymers remained close to the original end of reaction of the non-fluorinated polyurethane, which is attributed to the similar degradation onset of the fluorinated polyol to that of PTMG.

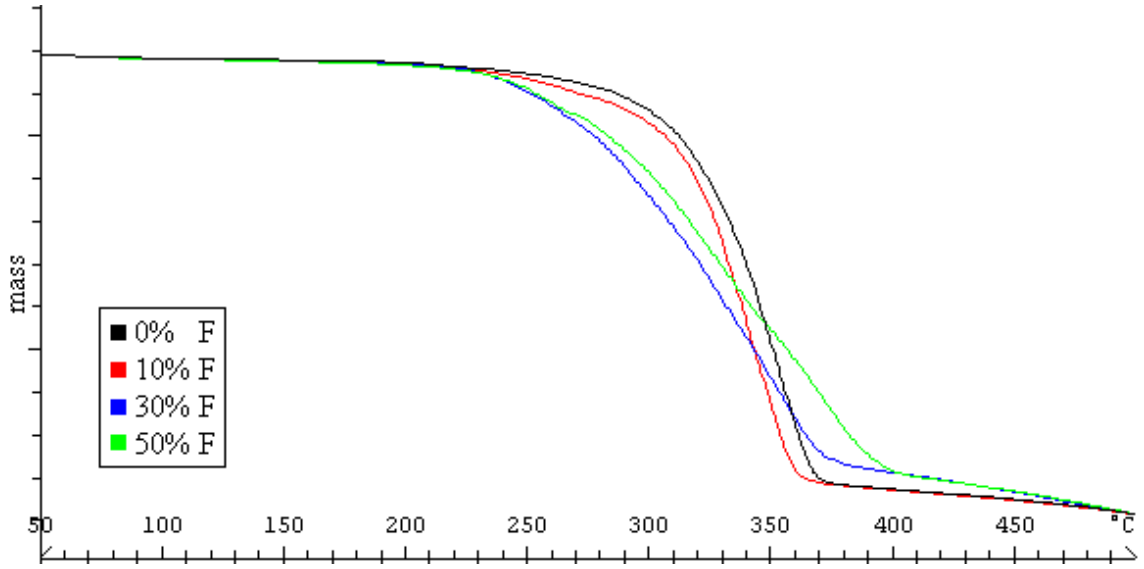


Figure 4.4.2. TGA curves for PPG based polymers with varying percentage of fluorinated soft segments, unexposed samples.

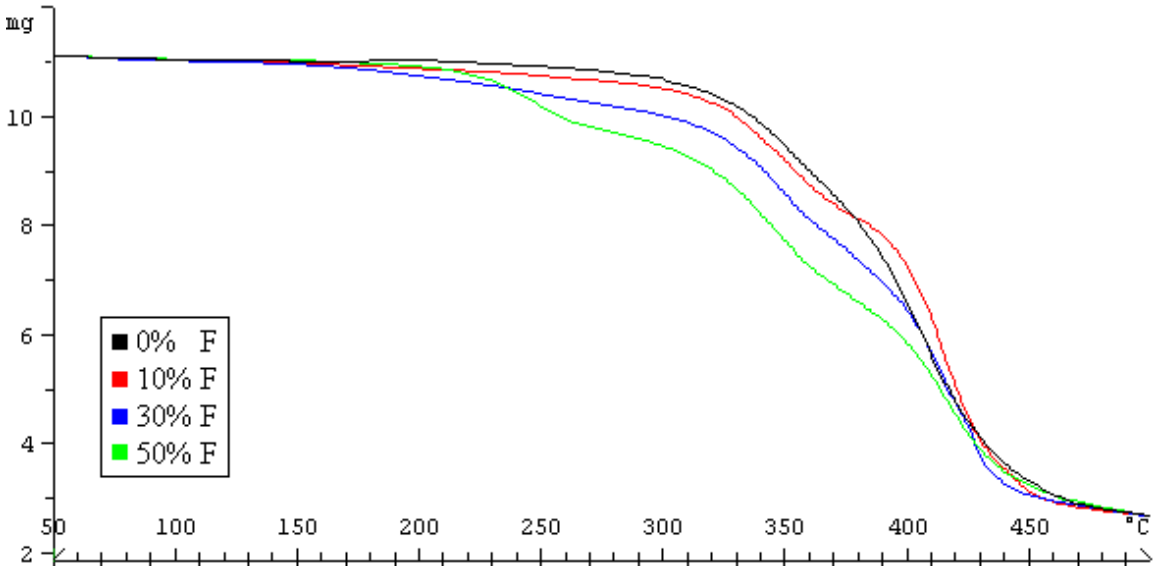


Figure 4.4.3. TGA curves of PTMG based polymers with varying percentage of fluorinated soft segments, unexposed samples.

4.5. Infrared Analysis

4.5.1. PTMG based polymers

Significant changes in some absorption bands were observed for the PTMG polymers, indicating the breakdown mechanism of these polymers. One of the most significant changes for the PTMG polymers happened in the carbonyl region. The relative intensities (rationed to the C-H stretching vibration at 3307cm^{-1}) increased almost 400% for the free carbonyl (1730cm^{-1}) and 600% for the H-bonded carbonyl (1710cm^{-1}), as seen on figure 4.5.1.1.

The significant increase in carbonyl is a strong evidence of oxidative degradation on these polymers. Polyether based polyurethanes are known for degrading on the ether segment causing chain scission and the generation of carbonyl groups. PTMG is not an exception, as the elevated temperature and presence of oxygen promotes the scission of the carbon atom next to the oxygen of ether (as shown on figure 4.5.1.2.), leading to the generation of a free radical that will propagate the oxidation.

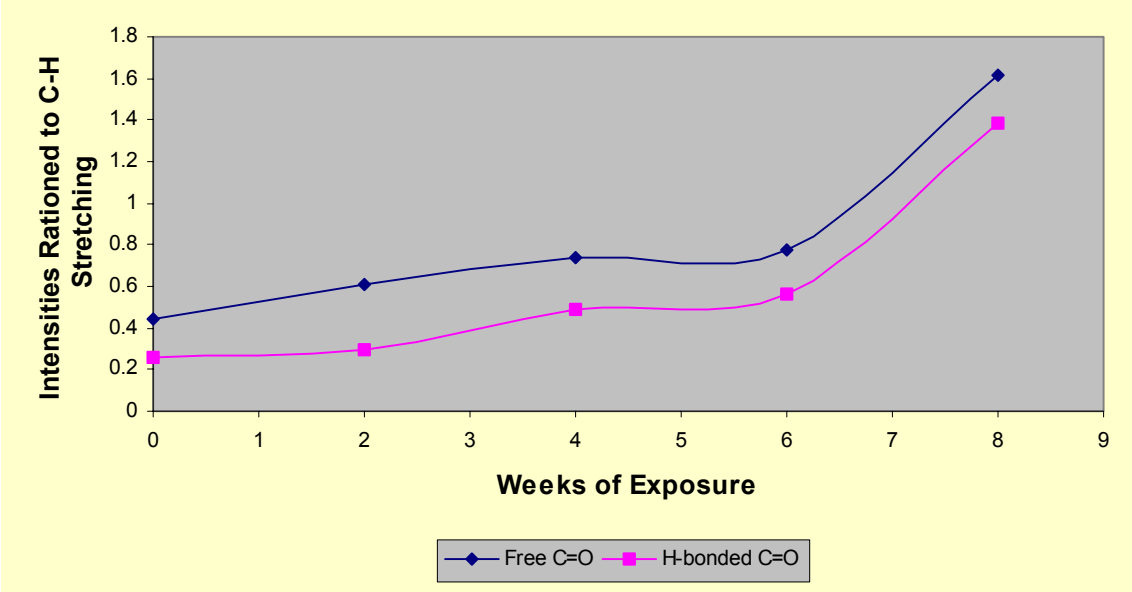


Figure 4.5.1.1. Relative intensities of carbonyl (1730 and 1710cm^{-1} wavelength) in non-fluorinated PTMG based polyurethane.

The ratio of the intensities of the free carbonyl to the H-bonded carbonyl (1730 by 1710 cm^{-1}) suggest that H-bonded carbonyls are forming in greater number than free carbonyl, or that some of the existing free carbonyls are bonding due to the increase in chain mobility after chain scission occurred, shown on figure 4.5.1.3. The important increase in the amount of hydrogen bonding of these polymers promotes a series of changes with respect to their mechanical behavior and morphology. Chains with very high hydrogen bonding density will encounter mobility restrictions, even after a considerable amount of chain scission. Considerations to the thermodynamics of the process would also have to be taken for assumptions regarding phase equilibria.

The presence of fluorinated soft segments changed the trend of the non-fluorinated PUs to a more constant ratio of free/H-bonded carbonyl along the exposure times. This is evidence that the presence of the fluorinated group affects the hydrogen bonding of the carbonyl groups, maintaining the ratio constant, is possibly due to the fact that carbonyl groups do not hydrogen bond as easily with the fluorinated segments (there are much less hydrogens in the fluorinated segments compared to the non-fluorinated polyglycols), reducing the chance of hydrogen bonding, as the shape of the relative intensities for the free and H-bonded carbonyl are similar (figures 4.5.1.4. and 4.5.1.5.). The 50% fluorinated PTMG based PU curves on figures 4.5.1.4. and 4.5.1.5.

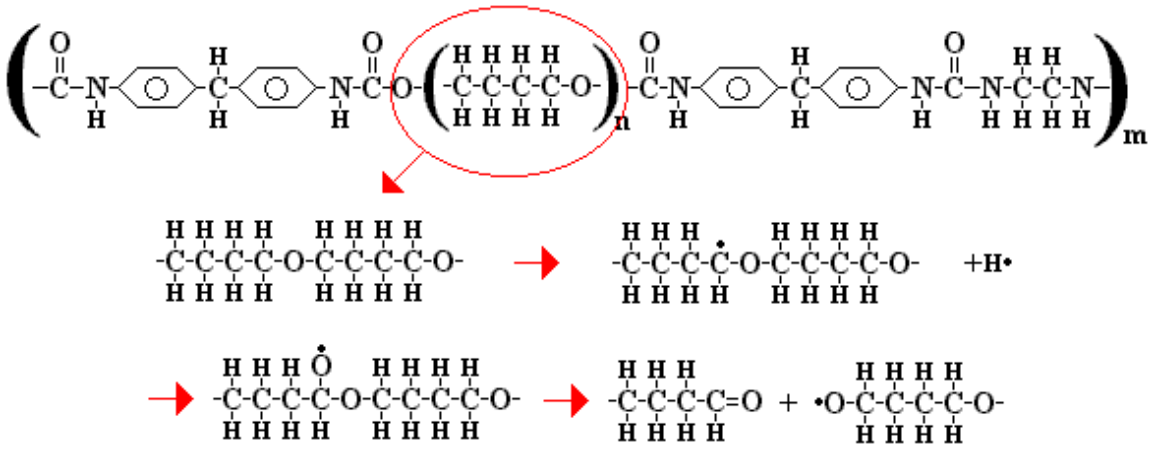


Figure 4.5.1.2. Suggested degradation mechanism for PTMG based polymers.

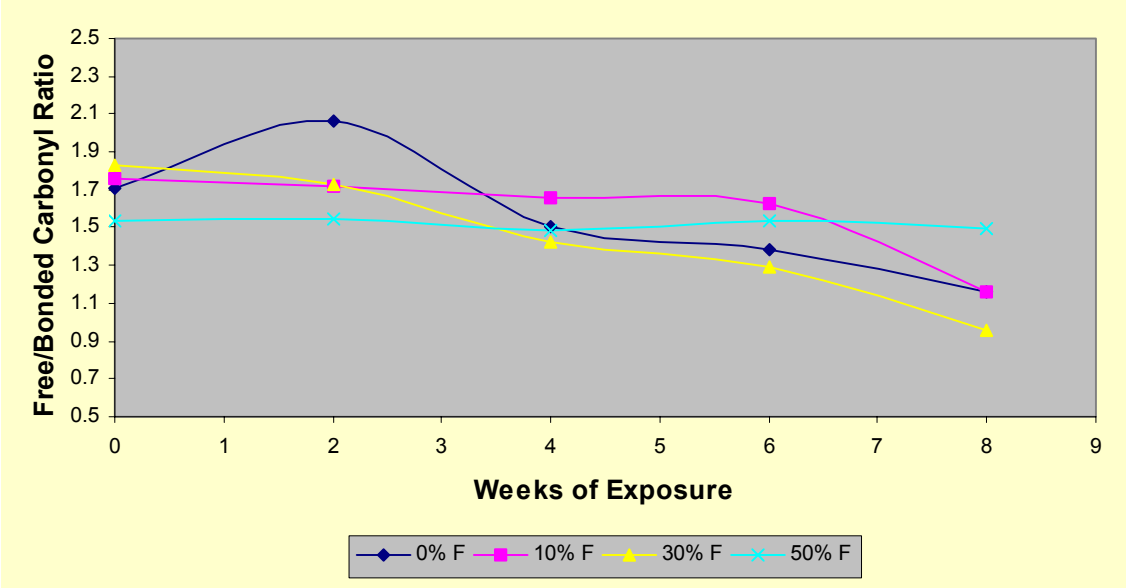


Figure 4.5.1.3. Free/H-bonded carbonyl absorptions for PTMG based polymers.

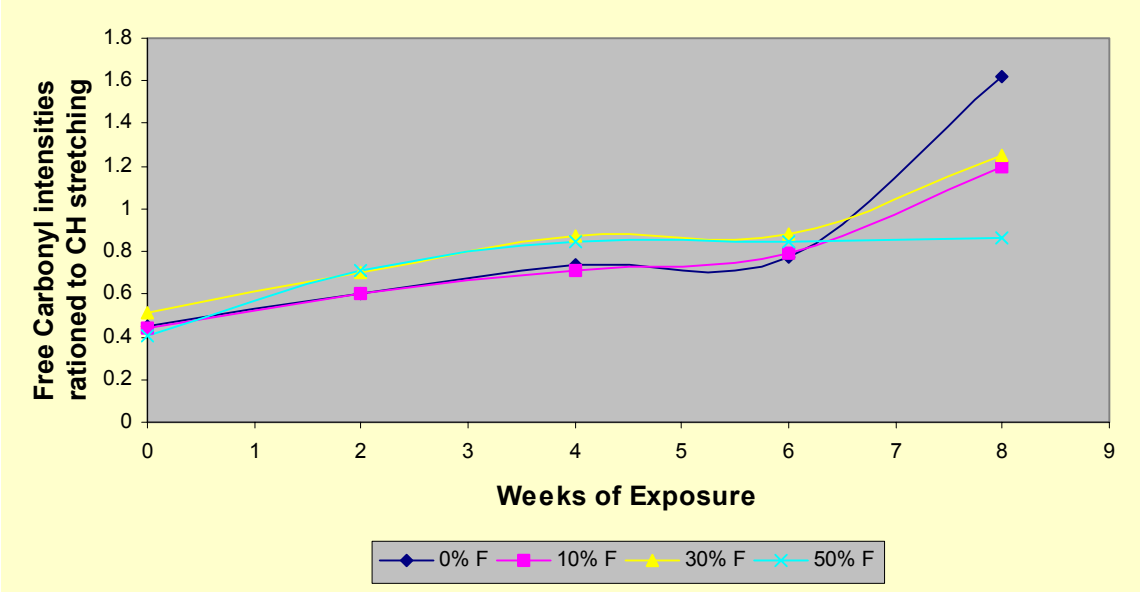


Figure 4.5.1.4. Relative intensities of free carbonyl for PTMG based polymers.

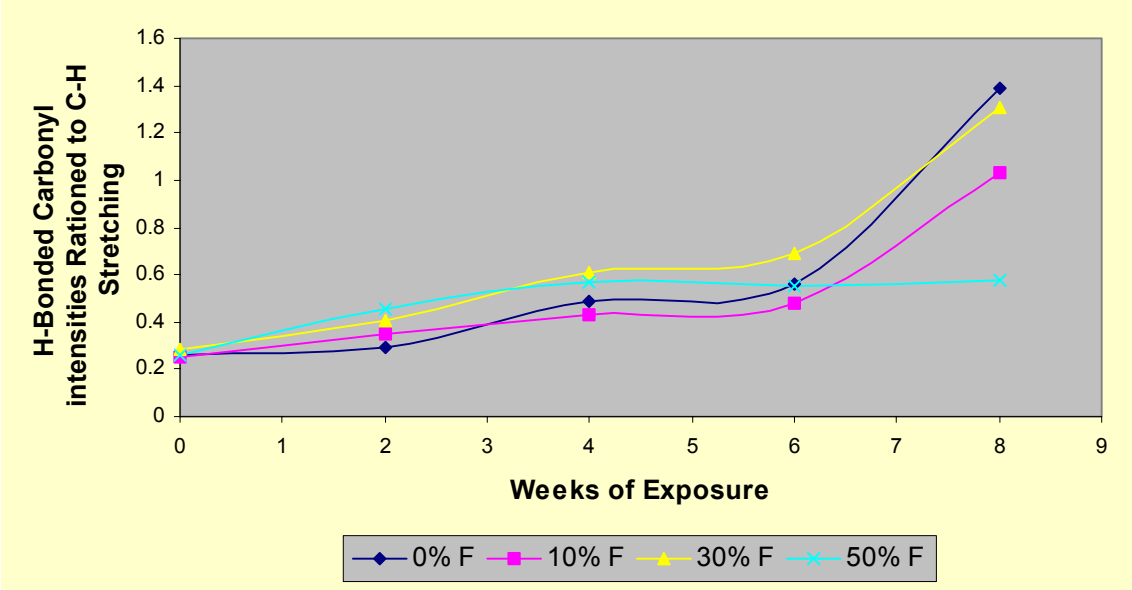


Figure 4.5.1.5. Relative intensities of H-bonded carbonyl for PTMG based polymers.

level off at exposure times above to 4 weeks. The 30% fluorinated PTMG based polyurethane, in the same two figures, levels at around four weeks and then jumps up at the final week, suggesting that the free and H-bonded carbonyl ratios are correlated for highly fluorinated PTMG based PUs. This behavior indicated that the oxidation for these polymers are associated with the ether segments, once the 50% fluorinated polymer tends to reduce this effect, while the other three presented similar results.

The urea carbonyl absorption shifted to lower wavenumbers with exposure time from 1649 to 1637cm^{-1}, as seen on table 4.5.1.1. The shifting of absorptions for urea carbonyl to smaller wavenumbers is generally associated with increase in H-bonding of these groups. This is reasonable, once chain scission leads to shorter chain segments and it facilitates the formation of hydrogen bonding. The relative intensities of the urea carbonyl and the urethane group (N(CO)) absorptions (1640 and 1730-1710cm^{-1}, respectively) did not change significantly with exposure time, implying in that the generation of carbonyl groups is restricted to the PTMG, under the exposure conditions. There was no shift (within experimental error) of the urea carbonyl absorption wave

Table 4.5.1.1. Absorption wavenumbers (cm^{-1}) for the urea carbonyl.

PTMG+	Unexposed	02 Weeks	04 Weeks	06 Weeks	08 Weeks
0% Fomblin	1649	1637	1637	1639	1638
10% Fomblin	1636	1635	1635	1635	1634
30% Fomblin	1633	1635	1636	1635	1633
50% Fomblin	1636	1635	1635	1635	1635

number for the fluorinated polymers ($1cm^{-1}$ for the 50% fluorinated versus $11cm^{-1}$ for the non-fluorinated), suggesting the shift is associated with changes in the PTMG segments. The smaller shift is attributed to the good thermal stability of the fluorinated segment as opposed of that of the PTMG.

The PTMG based PUs became insoluble in DMF after only two weeks of exposure (more on section 4.3.), but spectra of the insoluble portion of the sample and sample extract were collected with the use of an NaCl crystal. IR spectra of the sol fraction show very insignificant amount of H-bonded carbonyl, but very strong free carbonyl absorption in the $1730cm^{-1}$ region, as shown on figure 4.5.1.6. When compared to the extract, the spectra of the non-dissolved fraction contains both free and H-bonded carbonyl absorptions (1730 and $1710cm^{-1}$), as shown on figure 4.5.1.7., indication that free carbonyl containing chains dissolved readily while the H-bonded chains did not. For assurance that this effect is caused by hydrogen bondings, a stronger solvent such as DMSO would be used in the attempt to dissolve the polymers.

Figure 4.5.1.8. addresses the differences in the spectra of the non-fluorinated PTMG based PU with respect to aging. Note the substantial increase in absorption of the carbonyl groups, free and H-bonded (1730 and $1710cm^{-1}$). The changes in the $1289cm^{-1}$ region for the PTMG based PUs (figure 4.5.1.8.) is attributed to changes in the MDI hard segments, as the structures shown on figure 4.5.1.10. With aging, the PTMG based PUs became insoluble, as previously discussed, this is attributed to chemical crosslinking and increase in the H-bonded carbonyl groups. The changes in the benzene rings C-H stretching could be generating groups as quinoids, responsible for the yellowing of the

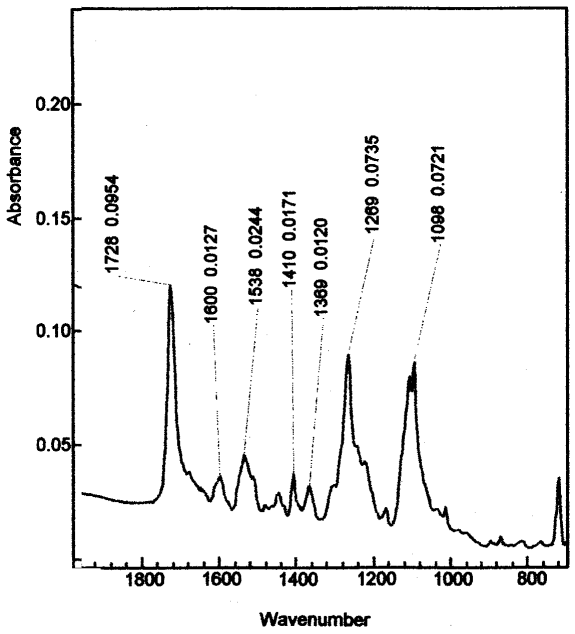


Figure 4.5.1.6. Spectra of the non-fluorinated PTMG based sample extract after eight weeks of exposure.

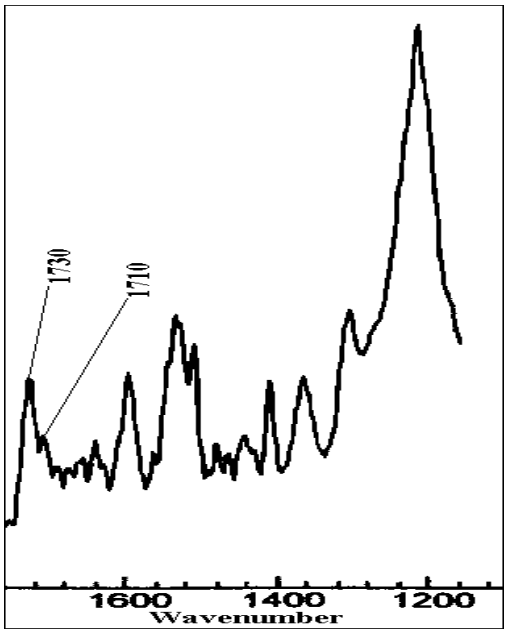


Figure 4.5.1.7. Spectra of non soluble in DMF portion of 50% fluorinated PTMG based sample exposed for 08 weeks.

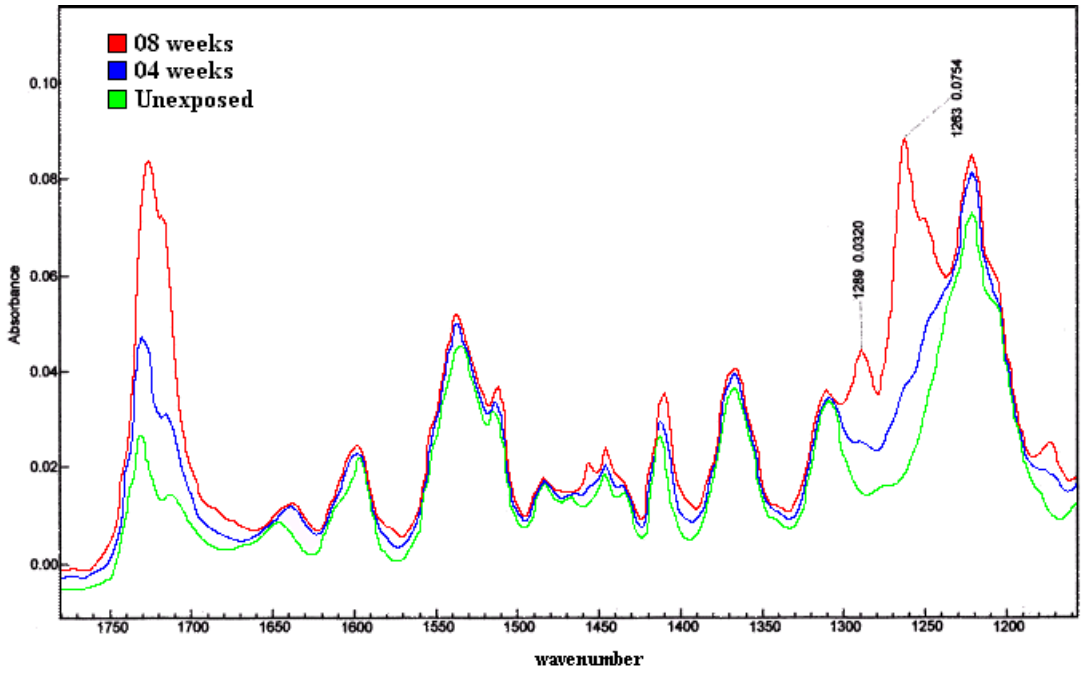


Figure 4.5.1.8. Spectra of PTMG based polymers, non-fluorinated, for different exposure times.

samples. Figure 4.5.1.9. shows the increase in the relative absorption of the benzene 1289cm^{-1} region along the exposure time of the non-fluorinated PTMG based PU.

The yellowing in PUs with aging are generally associated with changes in the hard segment (MDI) by two different pathways [40, 41, 42]. The first is associated with changes in the benzene ring with the formation of quinone-imides for samples exposed at ultraviolet light, not considered here. The second pathway is based on a series of reactions generating quinoid type structures by initial oxidation of the methylene carbon of MDI, as shown on figure 4.5.1.10. A strong indication of changes in the aromatic rings is the observed increase in scissoring and stretching of the aromatic rings double bonds absorption bands at around 1412 and 1598cm^{-1} respectively. The absorptions attributed to the scissoring and stretching of aromatic ring are shown on figures 4.5.1.11. and 4.5.1.12. Results show that the relative intensities for the non-exposed samples are very similar, while the intensities for the exposed samples increase with time. The presence of the fluorinated groups strengthens the tendency of the increase of double bonds in the aromatic rings. This may be due to the greater stability of the perfluorinated

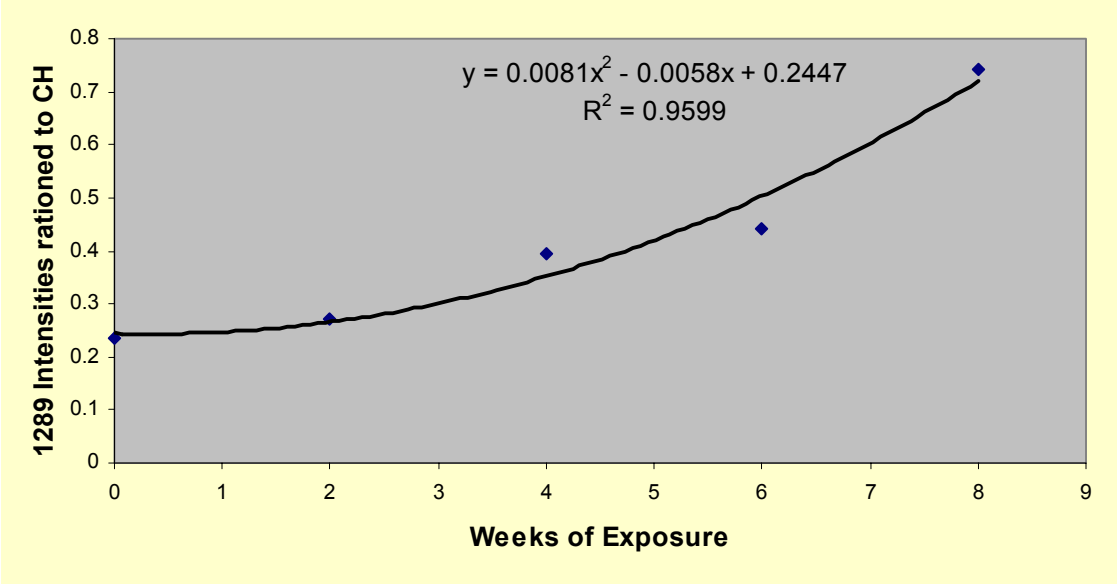


Figure 4.5.1.9. 1289cm-1 absorption for the 0%F PTMG based polymers.

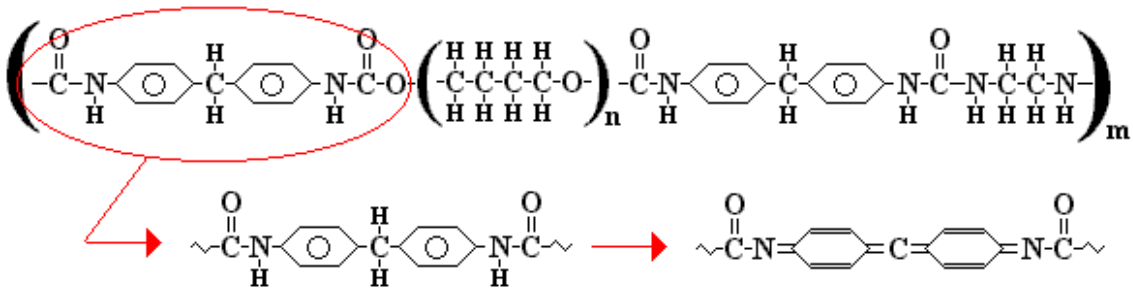


Figure 4.5.1.10. Reactions leading the formation of quinoids in MDI.

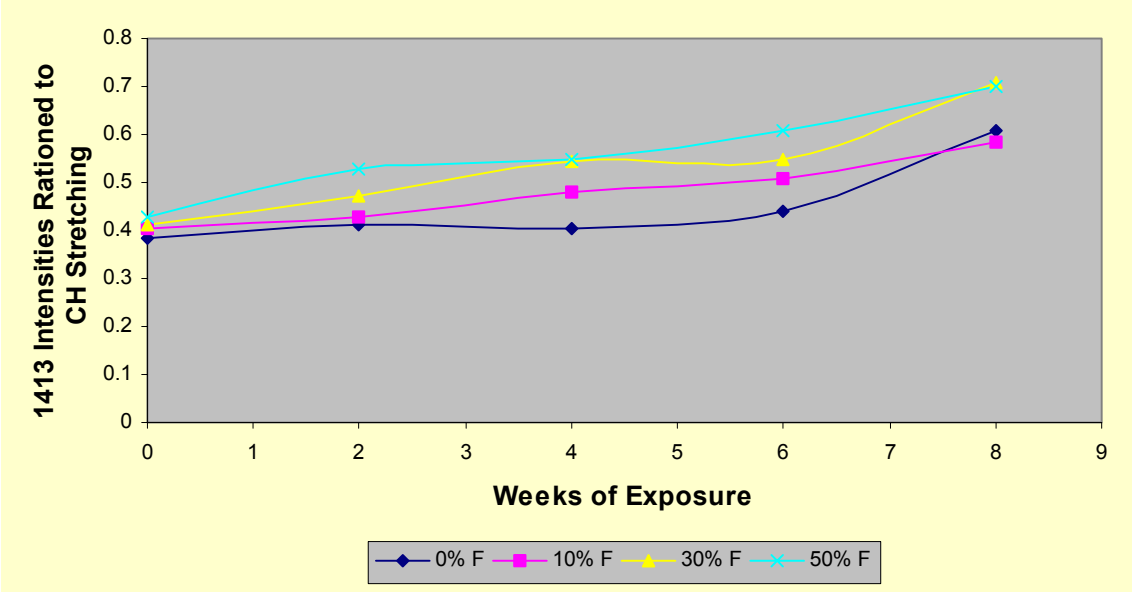


Figure 4.5.1.11. 1413cm-1 (C=C Scissoring in Aromatic Ring) for PTMG Polymers.

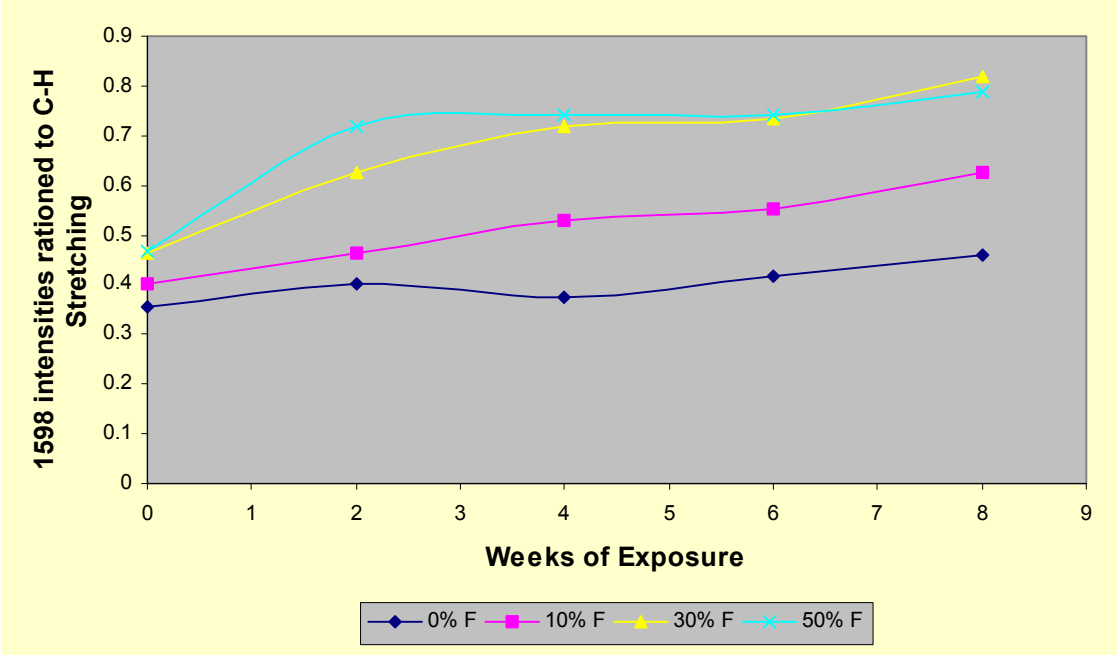


Figure 4.5.1.12. C=C stretching of aromatic ring for PTMG Based Polymers.

soft segment, allowing the MDI groups to absorb more available energy along with the non-fluorinated soft segments, as discussed earlier.

4.5.2. PPG based polymers

The changes observed for the PPG based polymer were subtle. According to Grassie and Scott [3.5.4.], the presence of the α-carbon on PPG is a challenge in the thermal processing of PPG containing polyurethanes, because the oxygen atom easily activates the carbon next to it, prompting oxidation and chain scission. The notorious tendency for the α-carbon of the PPG to oxidize is associated with the main degradation mechanism of these polymers. This is evidenced by the strong increase in relative intensity absorption in the free and H-bonded carbonyl (1730 and 1710cm^{-1}, respectively) with exposure time, as illustrated on Figure 4.5.2.2., which the intensities of the H-bonded carbonyl remains constant along the exposure, while the intensities of the free carbonyl significantly increases. This is due to the methyl side group that will make hydrogen bonding of the carbonyl groups difficult. Furthermore, the increasing number of free carbonyl (figure 4.5.2.2.) is a clear indication that oxidation will have a much more drastic effect on the material properties when compared to the PTMG based PUs.

While the free/H-bonded carbonyl ratios will significantly reduce for the non-fluorinated PTMG based PUs, they will sensibly increase for the PPG based PUs. This is due to the methyl group volume, that makes hydrogen bonding difficult, making the formed carbonyl groups (due to oxidation) raise the free/bonded ratio. The amount of free carbonyl is expected to promote changes in the sample's surface wettability once the surplus in carbonyl represents a surplus of oxygen (hydrophobic). The correlation of the relative free carbonyl absorption and the contact angle of the non-fluorinated PPG based PU is shown on figure 4.5.2.5. where the free carbonyl curve behaves in a very similar fashion to the contact angle..

Analogously to the PTMG based PUs, the relative intensity of H-bonded urea did not exhibit significant changes with exposure (figure 4.5.2.6.), but differently from the PTMG based polymers, there was no shifting observed for any of the PPG polymers in

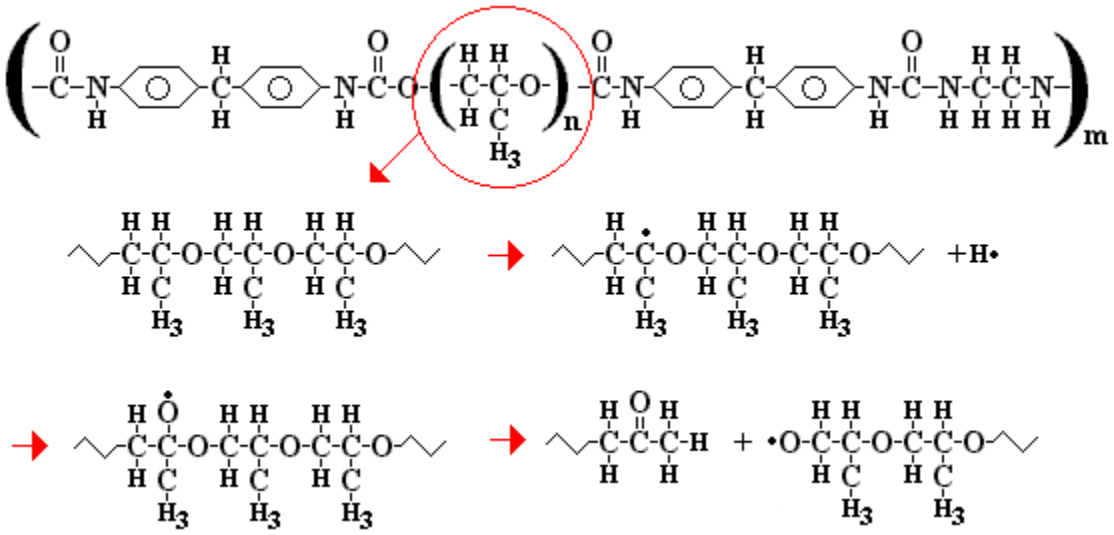


Figure 4.5.2.1. Oxidation mechanism of PPG based polymers.

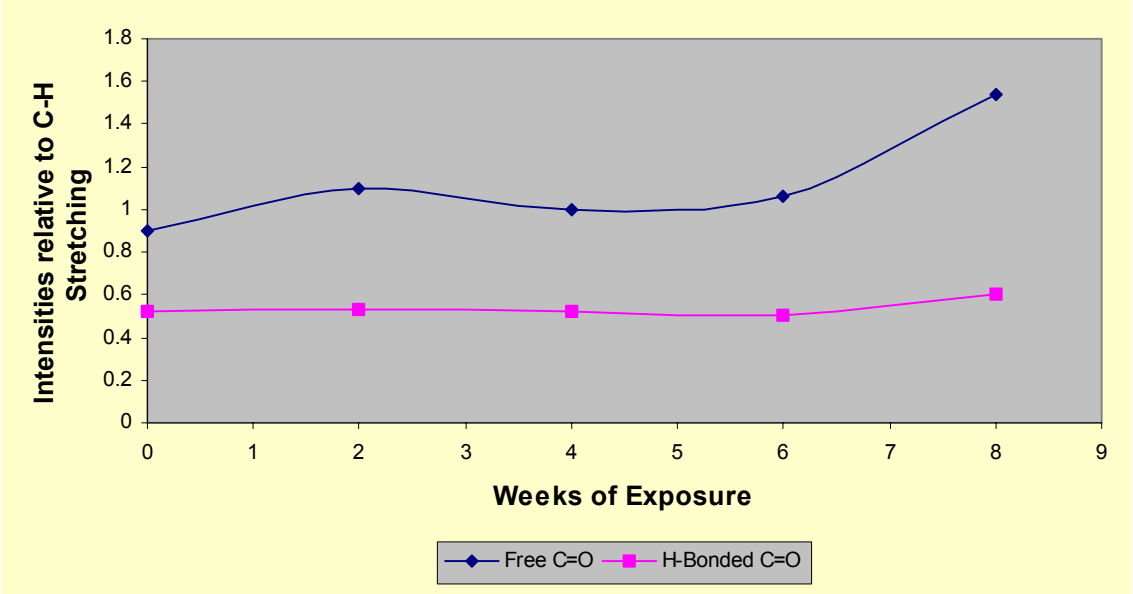


Figure 4.5.2.2. Relative intensities of free and H-bonded carbonyl for non-fluorinated PPG based samples.

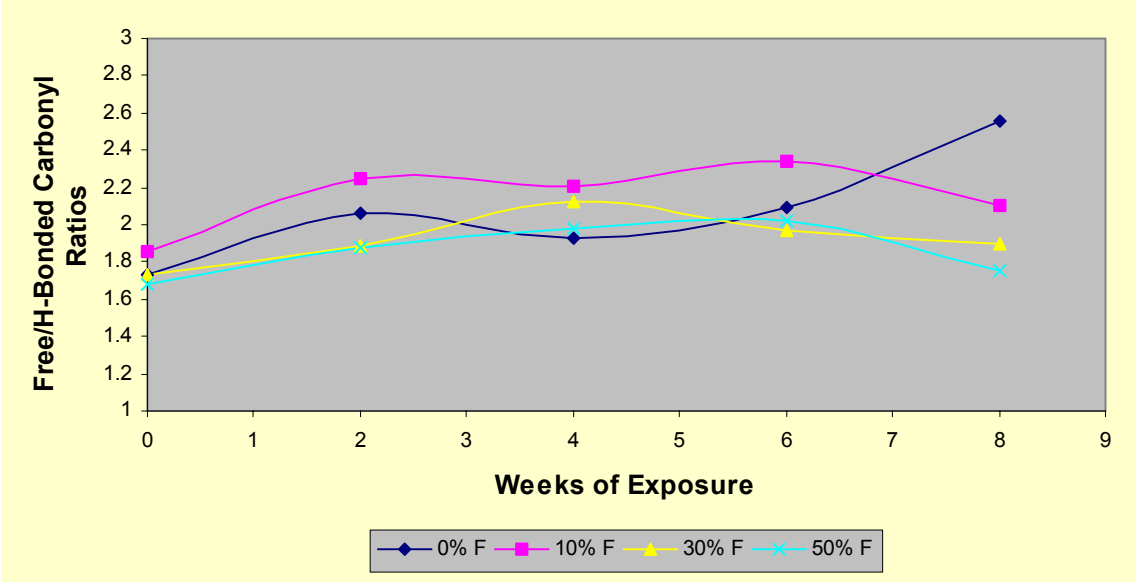


Figure 4.5.2.3. 1730 cm^{-1}/1710cm^{-1} ratios for PPG based polymers.

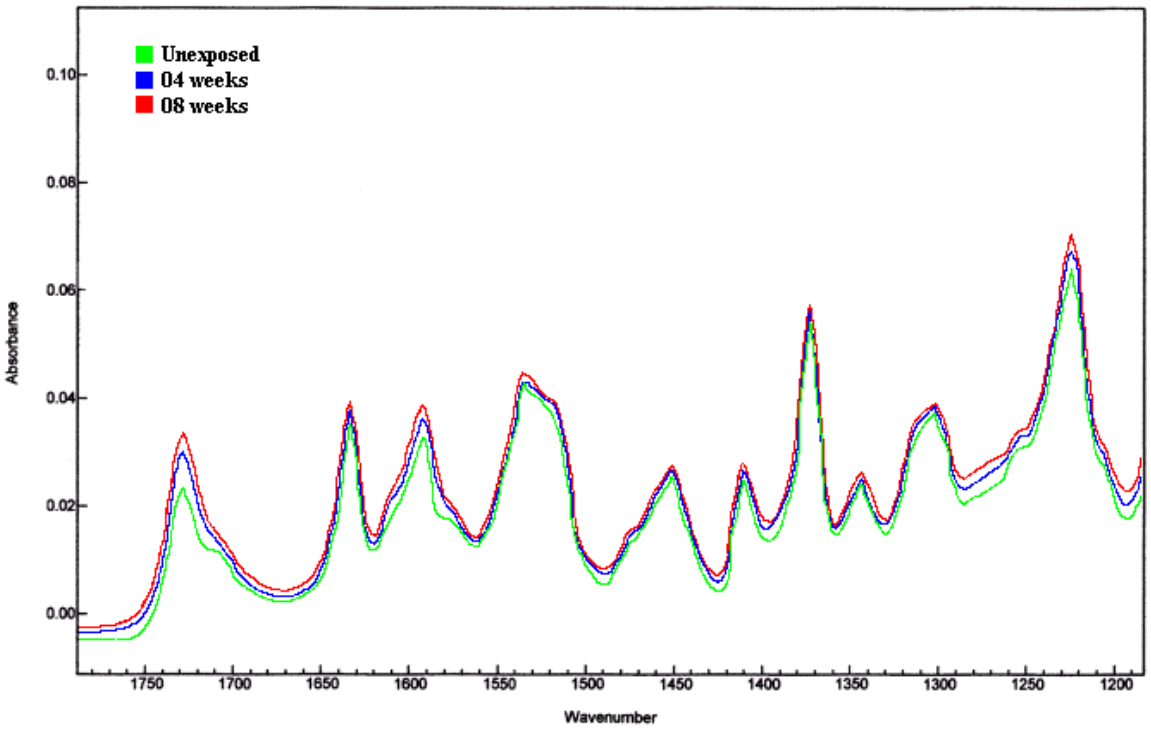


Figure 4.5.2.4. IR of PPG based polymers, 0% fluorinated soft segments, exposed for 0,4 and 8 weeks.

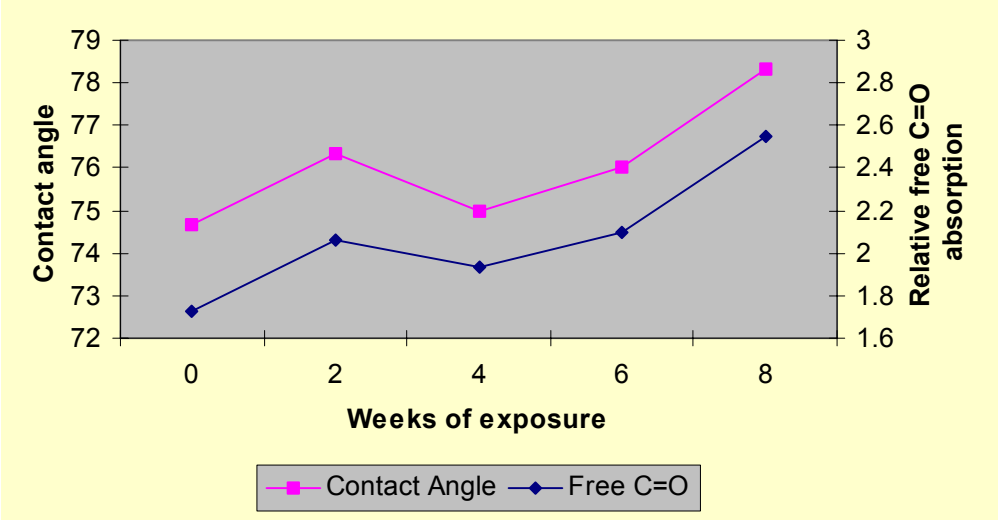


Figure 4.5.2.5. Contact angle and relative free PPG C=O absorption (rationed to C-H).

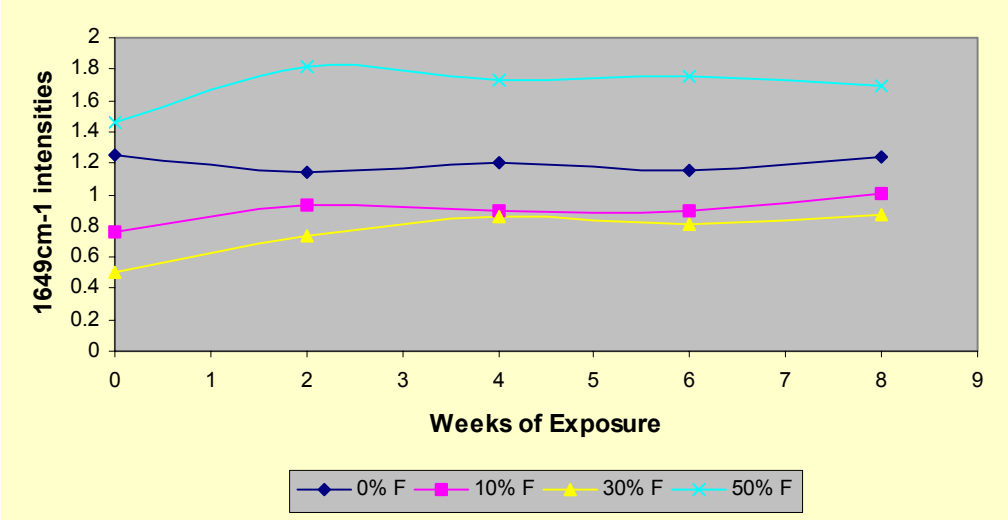


Figure 4.5.2.6. H-bonded urea carbonyl (1634cm^{-1}) intensities for PPG based polymers.

Table 4.5.2.1. Absorption wavenumbers (cm^{-1}) for the urea carbonyl.

PPG+	Unexposed	02 Weeks	04 Weeks	06 Weeks	08 Weeks
0% Fomblin®	1634	1634	1634	1634	1634
10% Fomblin®	1635	1634	1634	1634	1634
30% Fomblin®	1634	1633	1633	1633	1630
50% Fomblin®	1634	1634	1634	1634	1634

the urea carbonyl wavenumber. This may be due to the presence of the methyl group in the repeat unit of the soft segment, making it more difficult for the carbonyl groups to H-bond, then avoiding shifting of the absorption peak, as shown on table 4.5.2.1. The only exception in shifting observed for the PPG based samples was for the 30% fluorinated sample after eight weeks of exposure, but the shift is probably associated to the lower molecular weight of this specific polymer (shown on table 2.1.2.). The lower molecular weight of this material enhanced the molecular mobility allowing hydrogen bonding and the shift of the urea carbonyl (table 4.5.2.1.). Another significant change in relative absorption was in the (C=C) of aromatic rings (1590cm^{-1}), were an increase was noted for the highly fluorinated PUs, as shown on figure 4.5.2.7. This increase may be associated to the generation of quinoids (1412 and 1598cm^{-1} absorptions) due to the oxidation of the methylene group of MDI, shown on figure 4.5.1.10.

The presence of fluorine in the PPG based polymers influenced the results analogously to the PTMG based polymers with respect to the 1410cm^{-1} absorption band, attributed to the presence of quinoids and responsible for the deep yellowing with the exposure time. PPG based polymers presented very poor dynamic mechanical properties after exposure, much worse than the PTMG based PUs and this difference is attributed to the small free/H-bonded carbonyl ratios of the PPG based material.

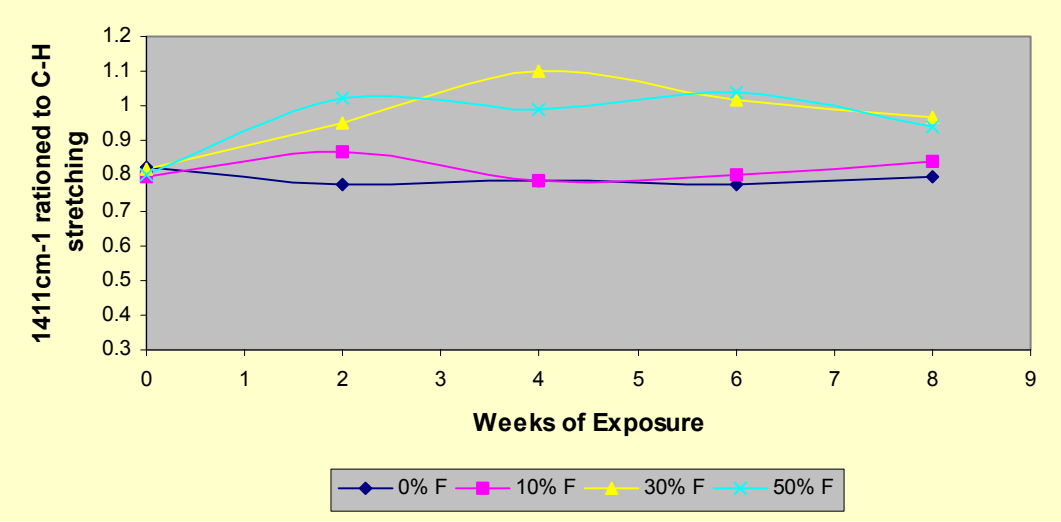


Figure 4.5.2.7. 1411cm^{-1} (C=C of aromatic rings) relative intensities for PPG PUs.

4.6. Dynamic Mechanical Analysis

Very significant changes were observed on the dynamic mechanical results, which will be addressed with respect to the chemical composition (soft segment type and degree of fluorination) and the exposure influence on these materials. Initially, two-dimensional composite curves were built using the 10Hz data of the test results presented on section 3.6. and Appendix C, which show analysis of the degree of fluorination and exposure times on the samples, as shown on figures 4.6.1. and 4.6.2. The Matlab® code used for the construction of the surface graphs shown in Appendix D and results for surface energies of glass transitions are shown in Appendix E.

Perfluorinated segments such as Fomblin® are often used as PUs additives for low temperature applications due to their very low glass transition. Fomblin Z-Dol 2000® has a glass transition of approximately –140^{o}C [2]. Note in figures 4.6.1. and 4.6.2., that the transition temperature of the fluorinated segment shifts to higher temperatures as the degree of fluorination increases (up to –112^{o}C). For ideally mixed fluorinated segments and PTMG segments, there would be a single transition for both components, but despite the similar solubility parameter of PPG, PTMG and Fomblin®, the transition temperature of the polyglycols and Fomblin® are too far apart to be merged into a single peak. Evidence that mixing at some extent happens, on the other hand, is the shifting of both transition temperatures to values intermediate to their initial values. In addition, note that the non fluorinated polymer (dark blue curve on figure 4.6.2.) shows slightly higher values of Tanδ in lower temperatures, attributed to segmented motions of the polyurethane chains, known to occur at approximately –150^{o}C. The three-dimensional plots shown on the results section are important when it comes to distinguishing noise from a real effect of the chemical structure on the Tanδ curve. In addition, the sequence of curves shown on figures C.18. to C.21. (Appendix C) show not only the increasing effect of Fomblin® on the –115^{o}C region, but that the small variations found on the 10Hz curves shown on figure 4.6.2. are noise, once it is only present at 10Hz. Figures C.22. to C.25. show the same effect on the PPG based samples. Figures 4.6.1. and 4.6.2. illustrate

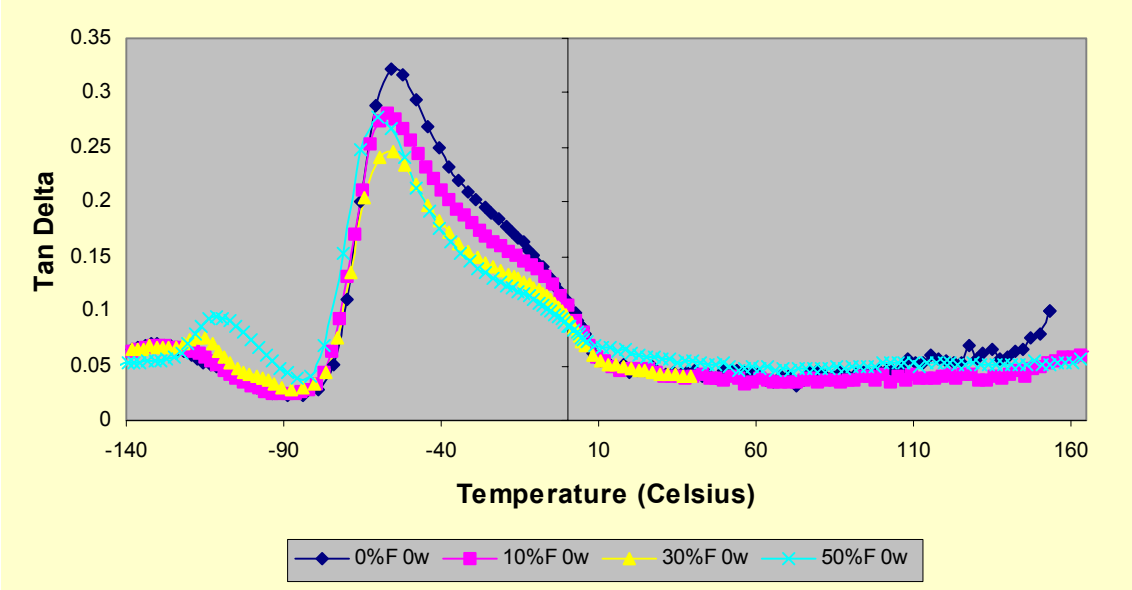


Figure 4.6.1. Tanδ of PTMG based polymers for varying degrees of fluorination. Values obtained from 10Hz frequency testing.

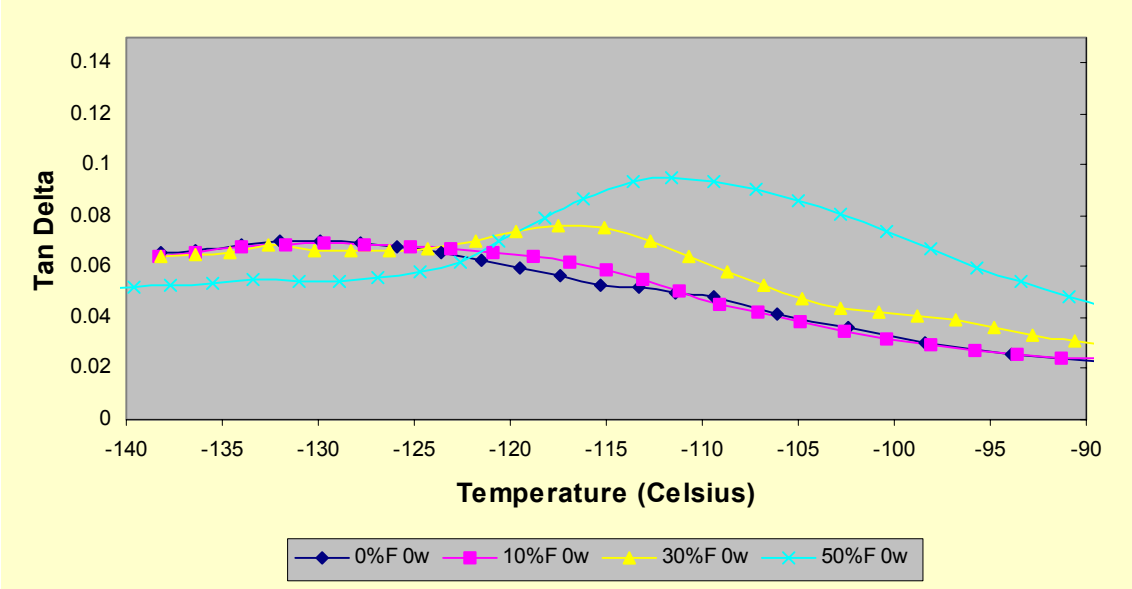


Figure 4.6.2. Tanδ of PTMG based polymers for varying degrees of fluorination, perfluorinated segment transition. Values obtained from 10Hz frequency testing.

the influence of the fluorinated segments in the main glass transition of the PTMG based PUs. The main relaxation, which occurs at around –50^{o}C is attributed to the Tg of the PTMG segments. In general, for the PTMG based PUs, the main Tanδ peak shifts to lower temperatures for increasing fluorination. This is attributed to the influence of the fluorinated segment on PTMG, as the two are expected to be miscible into some extent. The exposure time caused significant changes in the test results, especially for the loss modulus (and consequently Tanδ) of the PTMG based polymers (figure 4.6.3.). The values for E" around the main glass transition temperature of PTMG for the unexposed samples are fairly steady until the end of test. For the exposed samples, on the other hand, the appearance of the curves change dramatically, with high values for Tanδ, especially for higher frequencies, as illustrated for instance, on figures C.18. to C.21. (unexposed samples), on figures C.42. to C.45. (exposed for 02 weeks) and on figures C.66. to C.69. (exposed for 08 weeks). The non exposed PTMG based samples do not show the high values for Tanδ above the main transition, but after two and mostly after eight weeks of exposure, a very significant change occurs on this region, especially for the polymers with low degree of fluorination. Note that this trend is reduced when the amount of fluorinated soft segments increases, suggesting this phenomena is associated with PTMG. As PTMG is susceptible to forming small crystalline domains for MWs above 1700 (the one studied is 2000), the peaks in the loss modulus (Tm=15^{o}C, check appendix E for more information) tests are related to the melting of the crystalline domain. The effect of frequency on E" at temperatures close to the melting of PTMG is that for lower frequencies (lower strain rates), the sample is able to absorb the deformation without the rupture of hydrogen bondings, considering a high amount of hydrogen bonds is present on the PTMG segments. For the high strain rates (high frequencies), the sample is more likely to give way to the strain and absorb the energy applied by braking the H-bonds. The noise associated with this region strengthens the hypothesis of loss of crystalline domains and the presence of fluorinated segments would significantly reduce the degree of crystallization, further validating the hypothesis. Preliminary X-ray diffraction tests suggest that there is no crystalline domain at room temperature (Tm~15^{o}C, DSC curve on Appendix E).

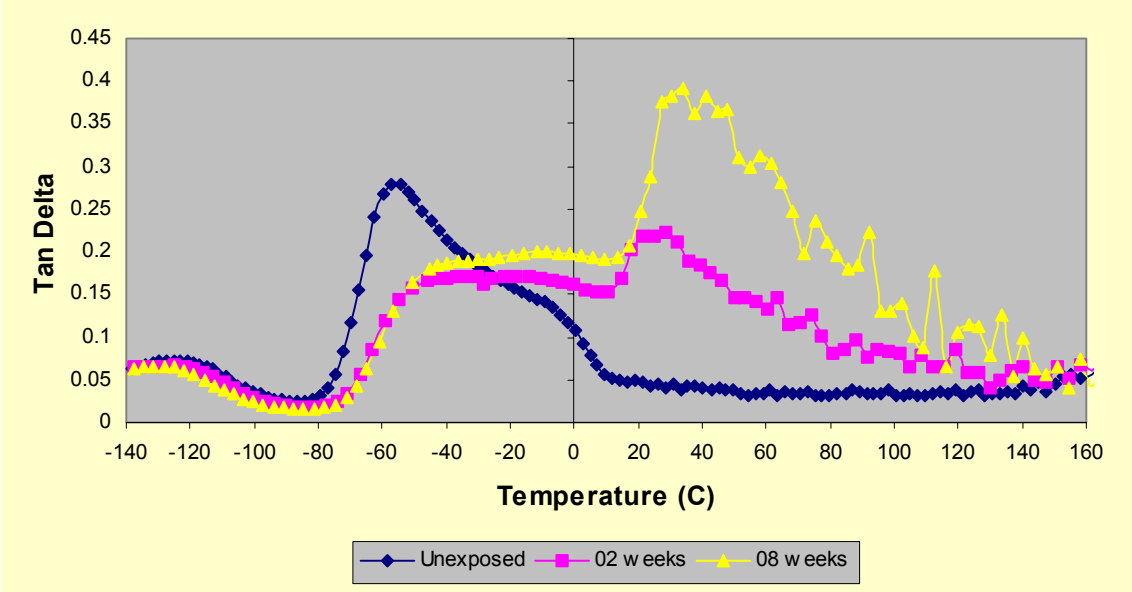


Figure 4.6.3. Tan delta of PTMG based polymers, 10% fluorinated soft segments, according to exposure times.

The increase in crystallinity due to changes in the morphology or chemical structure of a polymer is called chemi-crystallization [14]. The oxidation of polymers generally cause at least some chain scission and therefore an increase in chain mobility. As PTMG has the tendency to crystallize, increase in chain mobility would certainly cause some crystallization to occur, increasing the overall degree of crystallization of the polymer. The increase in crystallinity for the non fluorinated PTMG based material is shown on appendix F, which contains DSC scans of the non-fluorinated and10% fluorinated PTMG based PUs. Results show that the melting energy increased significantly from the non-exposed materials, a good indication of gain in crystallinity.

The value (height) and width of Tanδ peaks are associated with structural homogeneity and chain mobility [43]. In the case of polyurethanes, crosslinking or hydrogen bonding often decreases Tanδ values of peak and increase the peak breadth on glass transition. A broad molecular weight distribution would also cause peak breadth to increase. Figure 4.6.3. shows a drastic increase in peak breadth and a very significant Tanδ value decrease with the exposure time, a trend observed for all PTMG based

polymers. As the fluorination increases, the effects of degradation (although still very visible) present an important decrease, as shown on figure 4.6.4. for the 50% fluorinated PTMG PU. The same figure also shows an important shift in the glass transition of the fluorinated segment to lower temperatures, indication of further separation of the PTMG segments and fluorinated segment. This agrees with the hypothesis of enhanced crystallization of the soft segment, that would segregate the fluorinated segments from the newly formed crystals. The reduction of Tanδ could as well be associated with the restriction of movement of these groups due to the increase in cristallinity and possible crosslinking. This trend was appreciated for all PTMG based samples.

The transition temperatures were determined, for all polymers, according to the loss modulus peaks, as the peaks for Tanδ were not clear in some cases, especially for the aged PTMG based polymers. The results illustrate the influence of fluorination on the main glass transition, as shown on table 4.6.1. from the data at 10Hz. The glass transition temperatures (table 4.6.1.) show an important trend of increasing temperatures with exposure times, attributed to a possible increase in phase separation and due to the increase in hydrogen bonding density in the carbonyl groups (infrared analysis). This increase promotes chain mobility restrictions (a shift to higher Tgs).

The values presented on table 4.6.2. on the activation energies of the Tg of PTMG PUs show a general decrease with exposure times. A low activation energy implies in one of two things: a broader frequency influence on the loss modulus peaks, that means the transition temperature will shift more with varying frequencies than a material with high activation energy or in a lower transition temperature. The observed decrease in activation energies along exposure indicates that H-bonding does not influence significantly the Tg of PTMG based PUs, but it influences the melting region of the

Table 4.6.1. Main glass transition temperatures (Celsius) for PTMG based polymers.

	0% F	10% F	30% F	50% F
Unexposed	-65	-65	-65	-67
02 weeks	-64	-58	-59	-66
08 weeks	-51	-56	-57	-61

PTMG crystals. The carbonyl present in the PTMG crystals are closer to each other, being more likely to H-bond. The melting region of the PTMG crystalline phase presented an important change in terms of Tan δ. For increasing exposure times, a substantial relaxation is observed especially for the higher frequencies. The probability of H-bonding of the carbonyl groups on the crystalline phase of PTMG is very high due to the small distance of the groups. For this reason, the increase in hydrogen bonding density with exposure will affect the dynamic mechanical behavior of these polymers during their melting, promoting an increasing loss modulus at the higher frequencies due to the breakdown of these bonds for the higher strain rates, as observed in figure 4.6.4. This effect is reduced with increasing fluorination, indicating the correlation of this relaxation with PTMG. The activation energies for the melting relaxation (based on Tanδ curves) were determined and are summarized on table 4.6.3. The results show a much higher energy occurring on this transition than the energy of the breakdown of hydrogen bonds, what could be attributed to the energy used for the chain conformation after the bonds were broken.

The values for the activation energies of the Tg of the PPG based polyurethanes (table 4.6.4.) show a decrease with exposure times for the non-fluorinated and 50% fluorinated polyurethanes. For the others, activation energies dropped then recovered. A high activation energy, as discussed earlier, implies in less frequency influence in the E" peak shifting. PPG based polyurethanes in general have high activation energies when compared to PTMG polyurethanes, due mostly to the methylene side group on the soft segment, that makes the glass transition more energy consuming. The degradation influence on activation energies and Tg (table 4.6.5.) reflect the chain scission process due to the polymers thermal oxidation. An explanation for the shifting of the PPG based polyurethanes glass transitions is that chain scission reduces the restrictions for chain motions. Plots containing the activation energies of all polymers is included on appendix E. In polyurethanes the soft and hard domains tend to phase separate. During aging, chain scission promotes a shift of the Tg to higher temperatures, a competing effect to the chain mobility just described. Advanced degradation of the soft segment enhances phase

Table 4.6.2. Activation energies (kJ/mol) of PTMG based polymers Tg.

	0% F	10% F	30% F	50% F
Unexposed	112.4	95.2	102.1	89.4
02 weeks	112.6	92.9	79.3	71.3
08 weeks	79.0	89.0	78	121.0

Table 4.6.3. Activation energies (kJ/mol) of PTMG crystalline phase transition, samples exposed for 08 weeks.

0%F	10%F	30%F	50%F
131	152	210	429

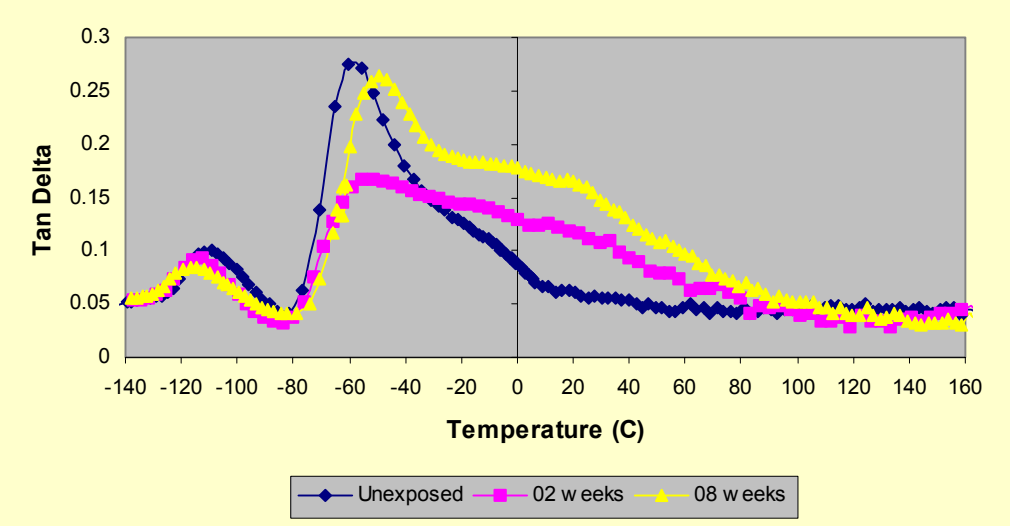


Figure 4.6.4. Tanδ of 50% fluorinated PTMG based polymers along to exposure times.

Table 4.6.4. Activation energies (kJ/mol) of PPG based polymers.

	0% F	10% F	30% F	50% F
Unexposed	110.0	126.0	136.0	106.4
02 weeks	108.9	116.7	109.3	142.2
Final week	94.4	134.5	131.0	109.1

Table 4.6.5. Glass transition temperatures (Celsius) for PPG based polyurethanes.

	0% F	10% F	30% F	50% F
Unexposed	-54	-53	-43	-49
02 weeks	-52	-57	-44	-50
Final week	-50	-52	-50	-54

separation, raising its Tg, while limited chain scission (as in the fluorinated samples) could lower the Tg due to gains in molecular mobility.

The effect of exposure time on E" for the PPG based samples are shown on figures 4.6.5. to 4.6.8. Note that on figure 4.6.5. the main Tg is in the –60 to –40^{o}C range (attributed to PPG) shifts to higher temperatures after degradation, while for increasing fluorination the Tg tends to decrease along the aging (Tgs are shown on table 4.6.5.).

An important observation about the mechanical behavior of the PPG based polymers is that these materials have a strong tendency to oxidize and therefore drastically affect the properties retention of the overall PPG based polyurethanes. Actually, the PPG based samples with 0 and 10% fluorination did not withstand 5g of dynamic load after the fourth week of exposure, the least required for a valid test in the equipment used. Consequently, the 30 and 50% fluorinated PPG polyurethanes exposed for eight weeks were compared with the 0 and 10% fluorinated PPG based polyurethanes exposed for 04 weeks. Thus, the 8th week of exposure was relabeled final week on tables 4.6.4., 4.6.5. and 4.6.6.

Results for the PPG polyurethanes breadth of half height of Tg illustrate the importance of polidispersity in the mechanical properties of polymers after aging. The 30% fluorinated PPG based PU presented lower Tg breadth of half height for all weeks (table 4.6.6.), due to this polymer's lower polydispersity (table 2.1.2.).

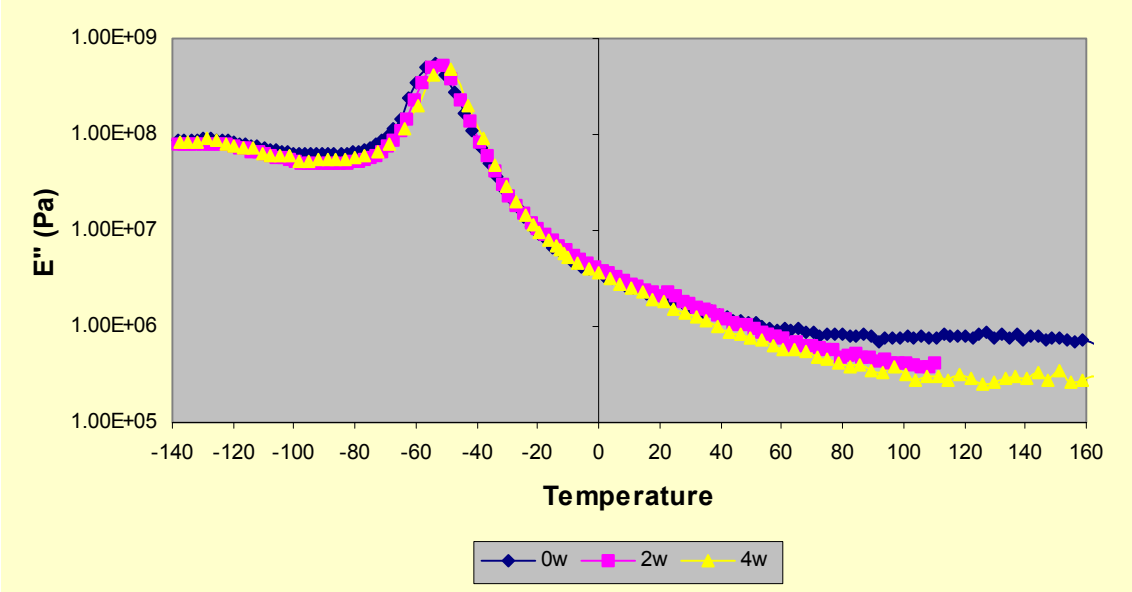


Figure 4.6.5. Loss modulus versus temperature for non fluorinated PPG based polymers.

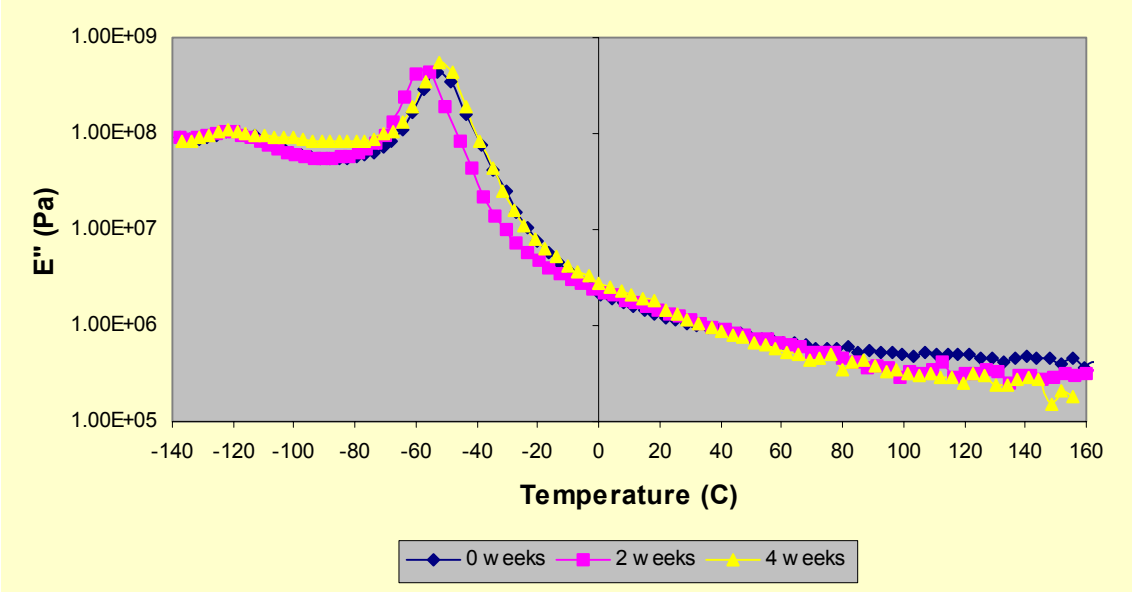


Figure 4.6.6. Loss modulus for the 10% fluorinated PPG based polymers.

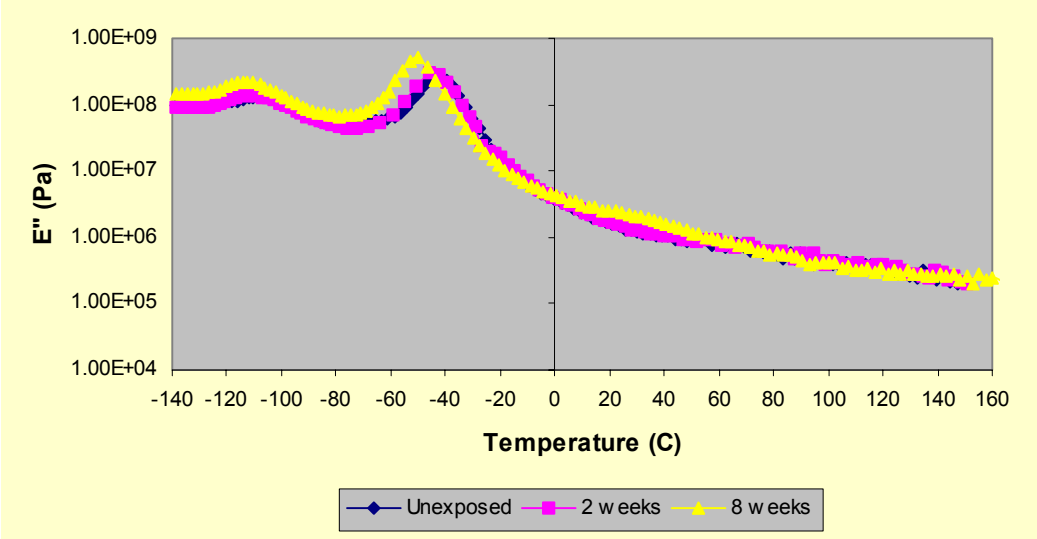


Figure 4.6.7. Loss modulus for 30% fluorinated PPG based polymers.

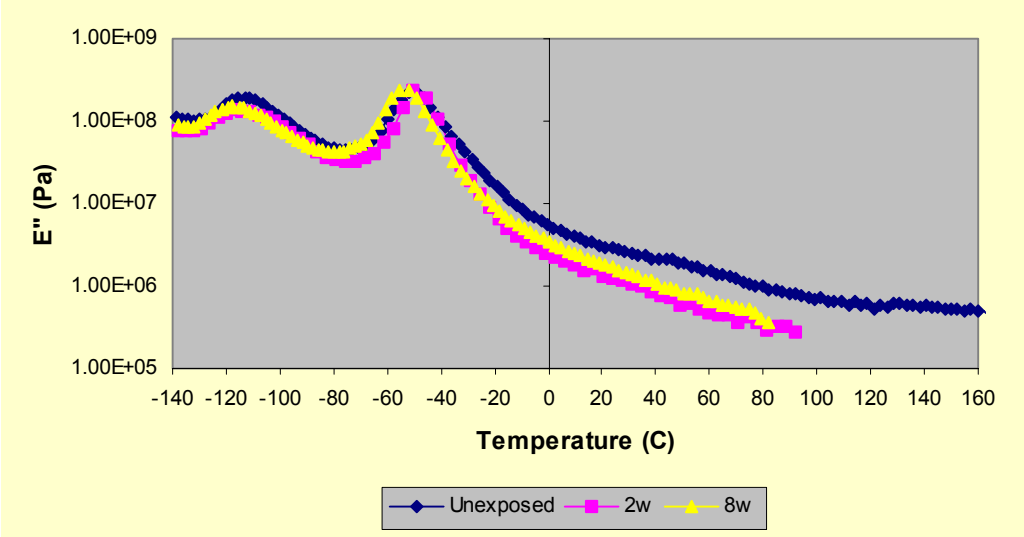


Figure 4.6.8. Loss modulus for 50% fluorinated PPG based polymers.

Table 4.6.6. Breadth of half height (degrees Celsius) of main Tg of PPG based polymers.

	0% F	10% F	30% F	50% F
Unexposed	29	29	27	35
02 weeks	29	27	23	30
Final week	28	26	24	32

5. Conclusions

Detailed examination of mass loss, contact angle, intrinsic viscosity, TGA, IR and DMA tests results revealed the mechanism of thermal oxidation of the studied polyurethanes in terms of type of soft segment, degree of fluorination and exposure time. Based on the results and discussion (chapters 3 and 4), the following conclusions were drawn:

1. The inclusion of thermally stable fluorinated segments in the chemistry of polyurethanes elastomers does not necessarily improve the thermal oxidative behavior of PTMG and PPG based polyurethanes. The presence of fluorinated soft segments can actually enhance the mass loss rate of non-fluorinated polyglycols that will be susceptible to chain scission. The inclusion of fluorinated segments increased the rate at which both groups of polyurethanes lost mass with exposure. Mass loss of the fluorinated polyurethanes studied is governed by the thermal oxidative stability of the soft segments. PPG as opposed to PTMG is more prone to oxidation, leading faster mass loss.

   In terms of non-isothermal degradation (TGA), the inclusion of fluorinated segments will also lower the degradation onset temperature, even though the degradation termination will be at a higher temperature. In terms of viscosity, the aged PPG based polyurethanes presented a significant drop, trend that was reduced with increasing degrees of fluorination. The PTMG based polyurethanes also presented reduced viscosity values with increasing degrees of fluorination, but these polymers did not dissolve after aging, effect of chemical crosslinking.
2. In terms of surface wettability, considering the main application of fluorinated polymers are in surface coatings, the inclusion of fluorinated segments increased the contact angle of the samples, even though the increase was only significant for the highly fluorinated polyurethanes. The PPG based polyurethanes initially presented lower contact angles when compared to the PTMG based Pus, but these materials behaved differently after aging. The amount of free carbonyl groups increased the contact angle in the PPG based PUs due to the oxygen's water

repellant forces. For this reason, the type of polyglycol will influence the contact angle of polyurethanes. The glycol that will generate more free carbonyl groups will become more hydrophobic with aging.

3. DMA results show the influence of the soft segment on the dynamic mechanical stability of the studied polyurethanes. Due to the high tendency of the PPG segment to oxidize and break down, the PPG based polyurethanes only stood for four weeks of exposure time, being too fragile after the fourth week to be tested. The PTMG based polyurethanes, on the other hand, withstood the eight weeks even though oxidation occurred significantly. The maintenance of the PTMG based Pus dynamic mechanical properties is attributed to two main factors:
    - Presence of chemical crosslinks due to exposure;
    - High density of hydrogen bonding in the carbonyl groups.

    DMA results show the transition temperature of the fluorinated soft segment (Fomblin®) shifting to higher temperatures with increasing degrees of fluorination. This shift is proof that the fluorinated and the non-fluorinated soft segments are mixing into some extent, but not completely. Aging moves the transition temperature of the non-fluorinated segments on the PTMG based polyurethanes to higher temperatures while for PPG based polyurethanes the shift occurs to lower temperatures.

6. Future Work

Future work which will contribute to the understanding of the thermal oxidative behavior of fluorinated polyurethanes include:

1. More detailed study of the molecular architecture along the thermal oxidative degradation of segmented polyurethanes.
2. The use of different temperatures in the exposure process would allow the construction of time-temperature superpositions, which could be used for the determination of the lifespan of these materials for specific applications.
3. The correlation between EDA and BTD derived PTMG fluorinated polyurethanes. BTD generates thermally processable polyurethane elastomers and studying the thermal-oxidation of these materials will add one more variable in the process due to the smaller number of hydrogen bondings.
4. The study of PTMG polyglycols and PPG polyglocols of molecular weights comparable to the studied polyurethanes would contribute to the understanding of onset in isothermal and non-isothermal degradation of PUs.
5. Thermal oxidative degradation study of polyurethanes based on different molecular weights polyglycols would clarify the effect of the soft segment length on the degradation kinetics.

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APPENDICES

Appendix A. TGA temperatures analysis.

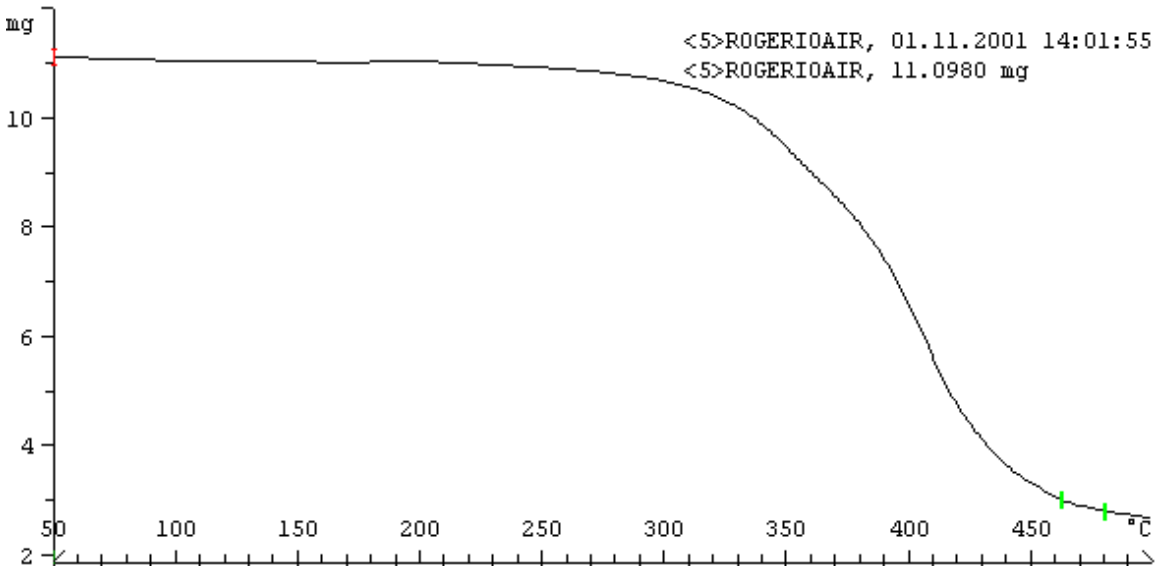

Figure A.1. PTMG based polymer, 0% fluorinated soft segment, unexposed.

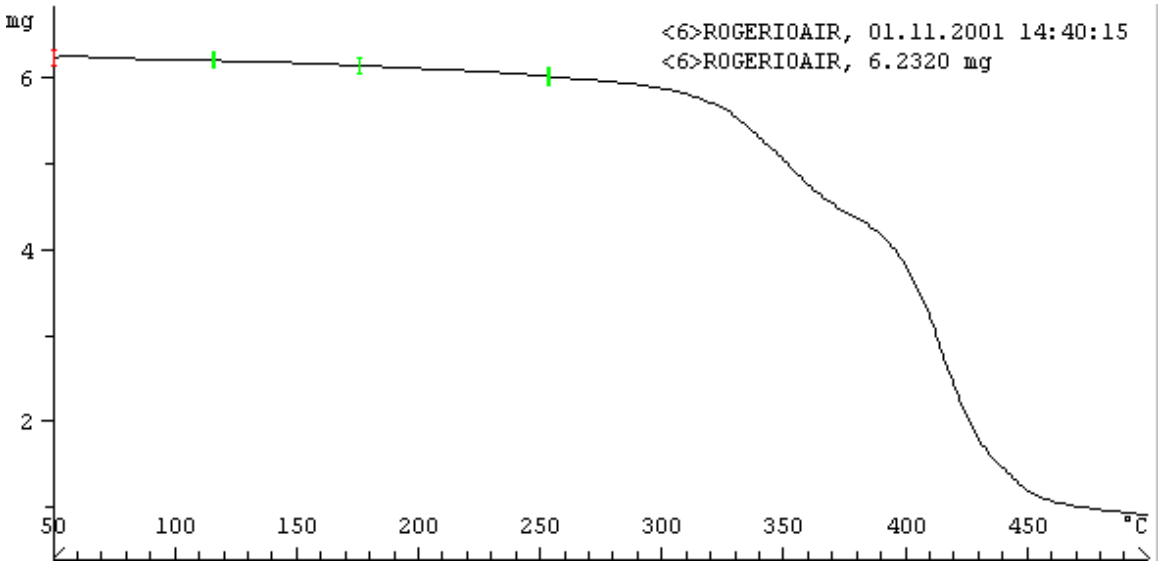

Figure A.2. PTMG based polymer, 10% fluorinated soft segment, unexposed.

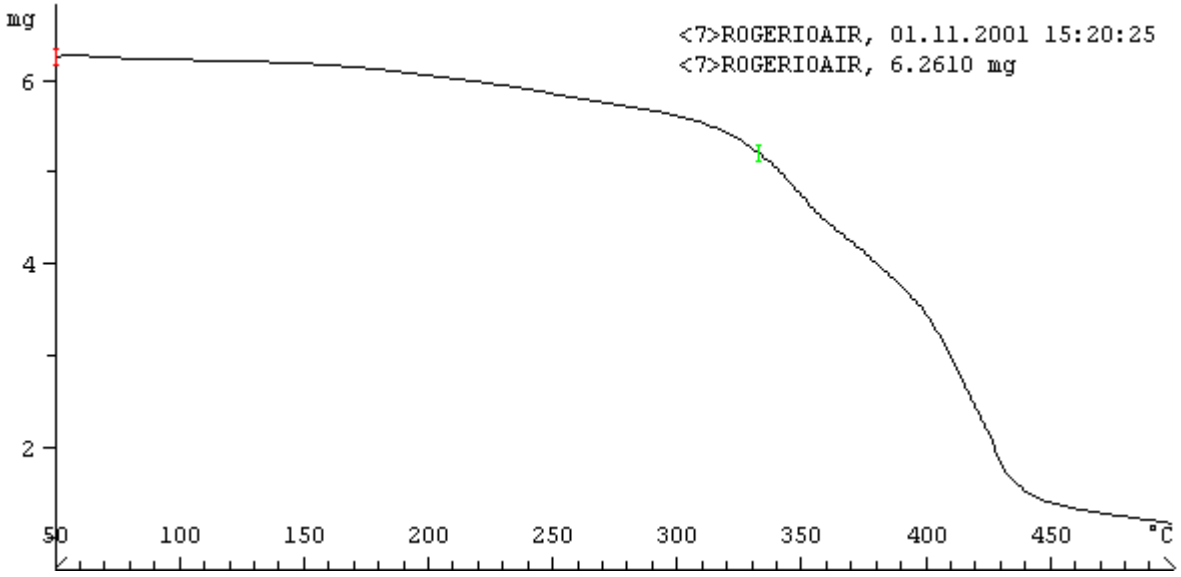

Figure A.3. PTMG based polymer, 30% fluorinated soft segment, unexposed.

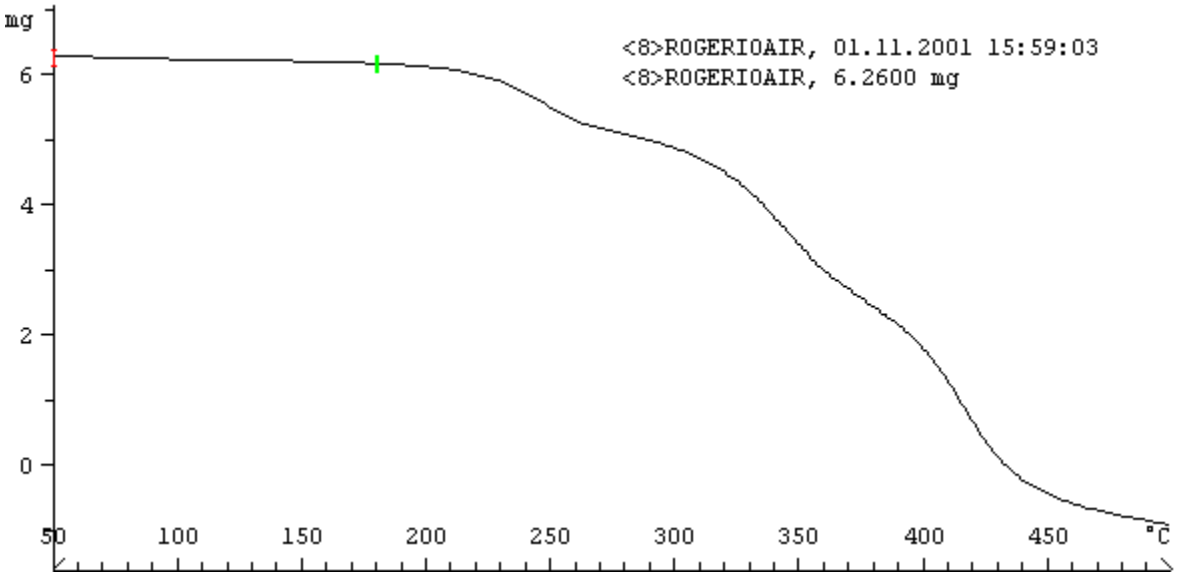

Figure A.4. PTMG based polymer, 50% fluorinated soft segment, unexposed.

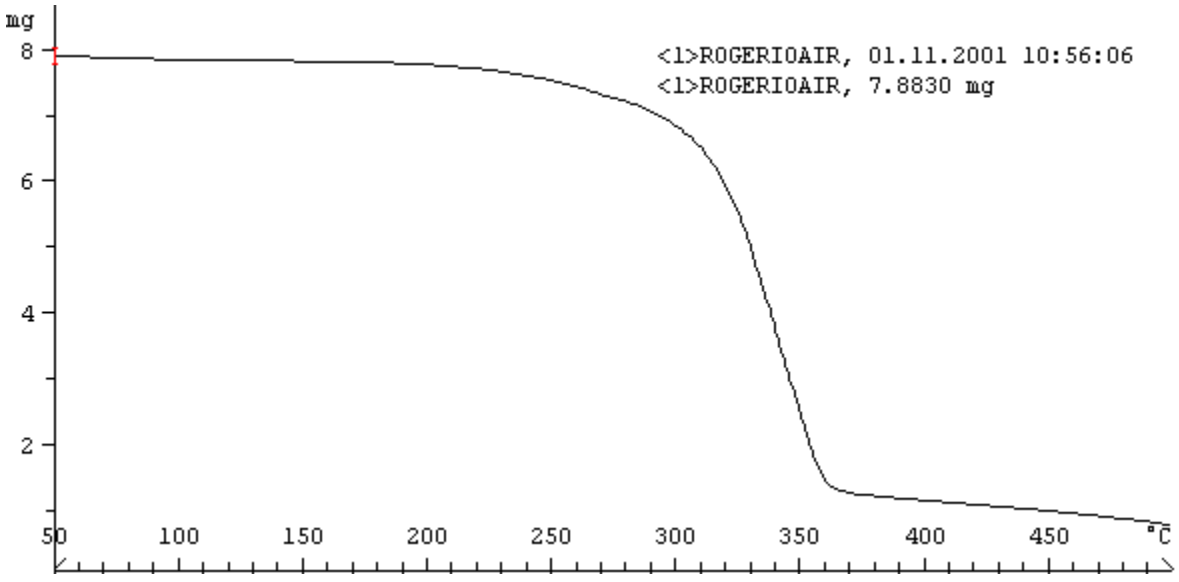

Figure A.5. PPG based sample, 0% fluorinated soft segment, unexposed.

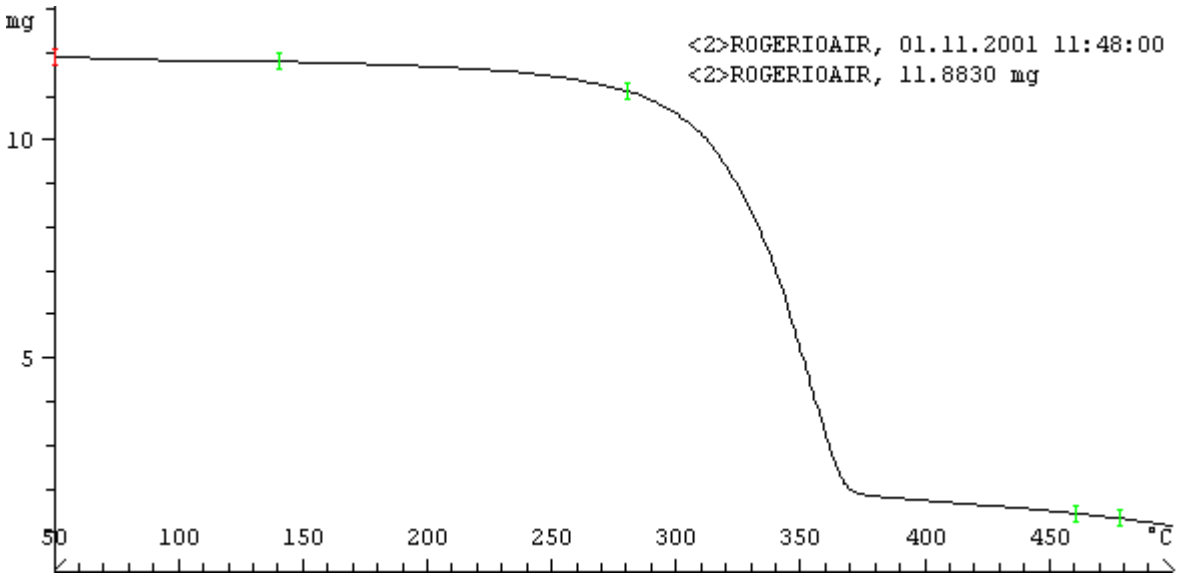

Figure A.6. PPG based polymer, 10% fluorinated soft segment, unexposed.

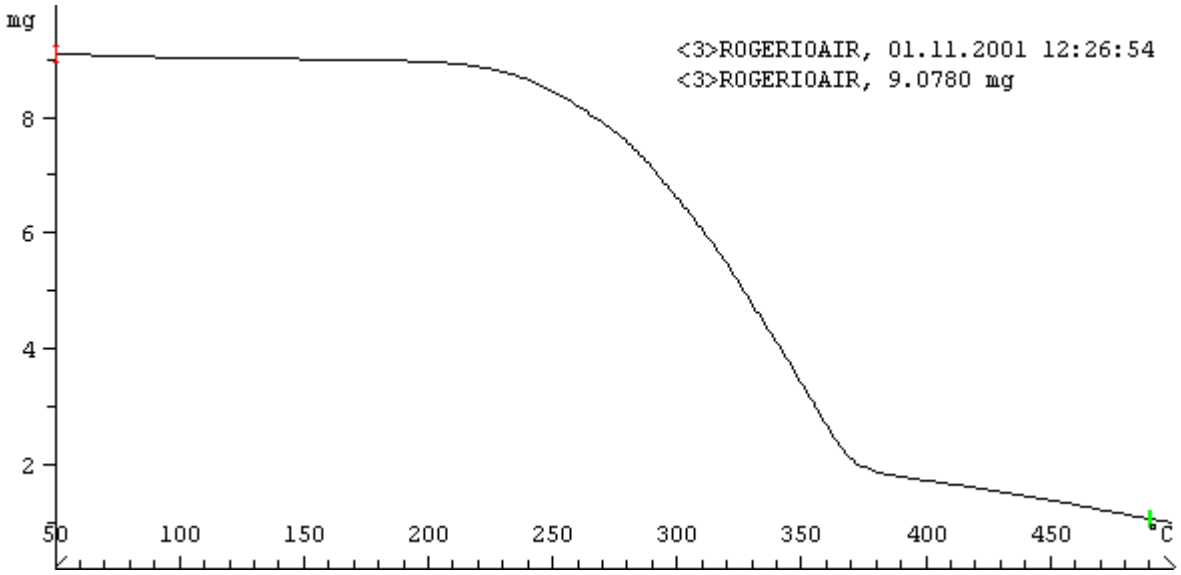

Figure A.7. PPG based polymer, 30% fluorinated soft segment, unexposed.

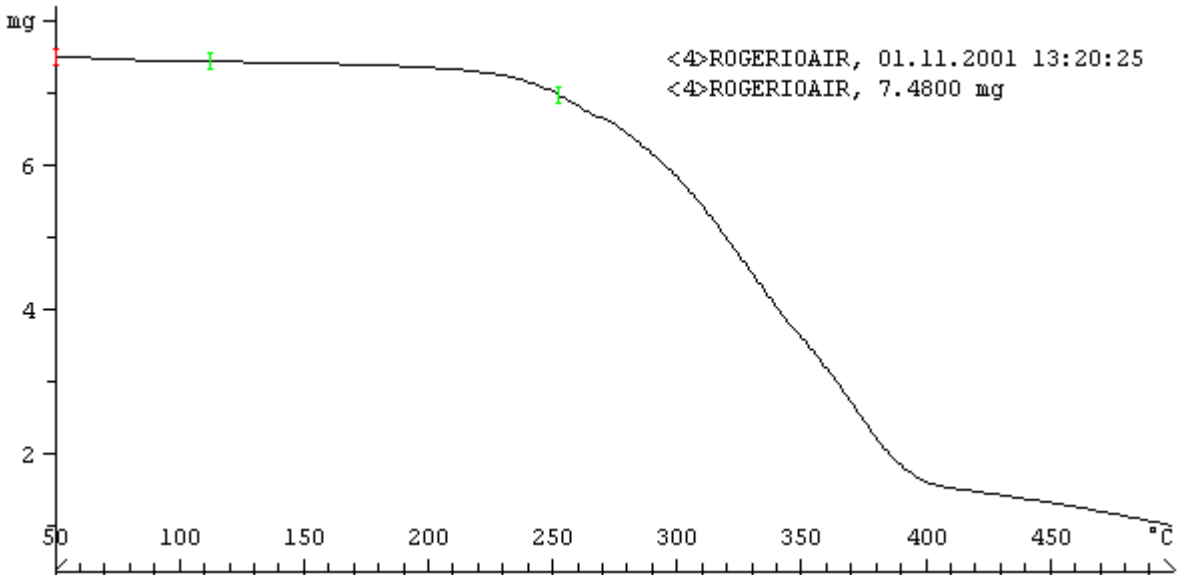

Figure A.8. PPG based polymer, 50% fluorinated soft segment, unexposed.

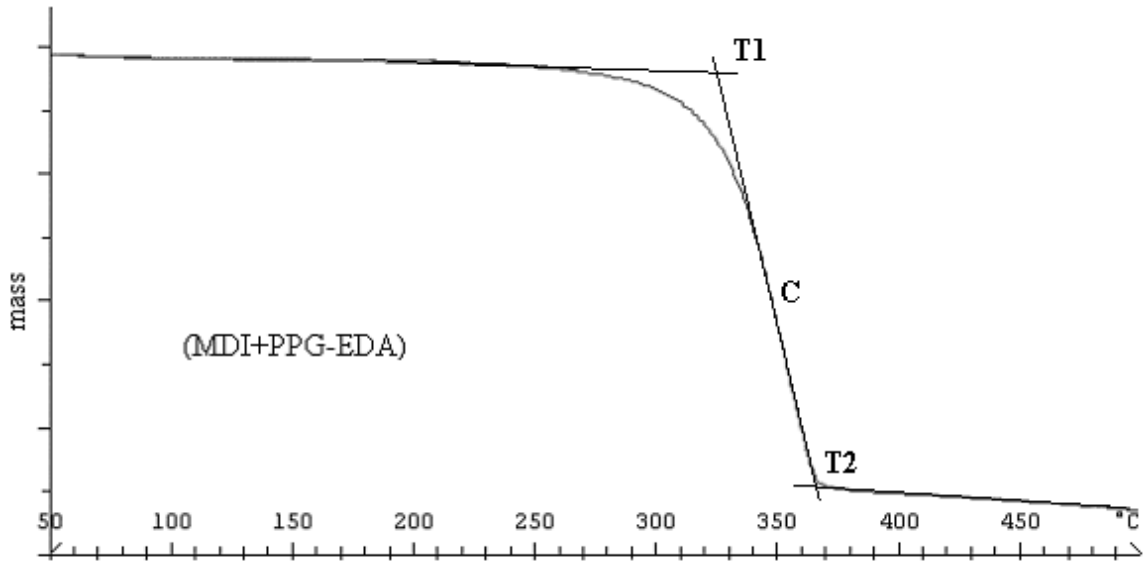

Figure A.9. MDI PPG EDA, non-fluorinated, unexposed.

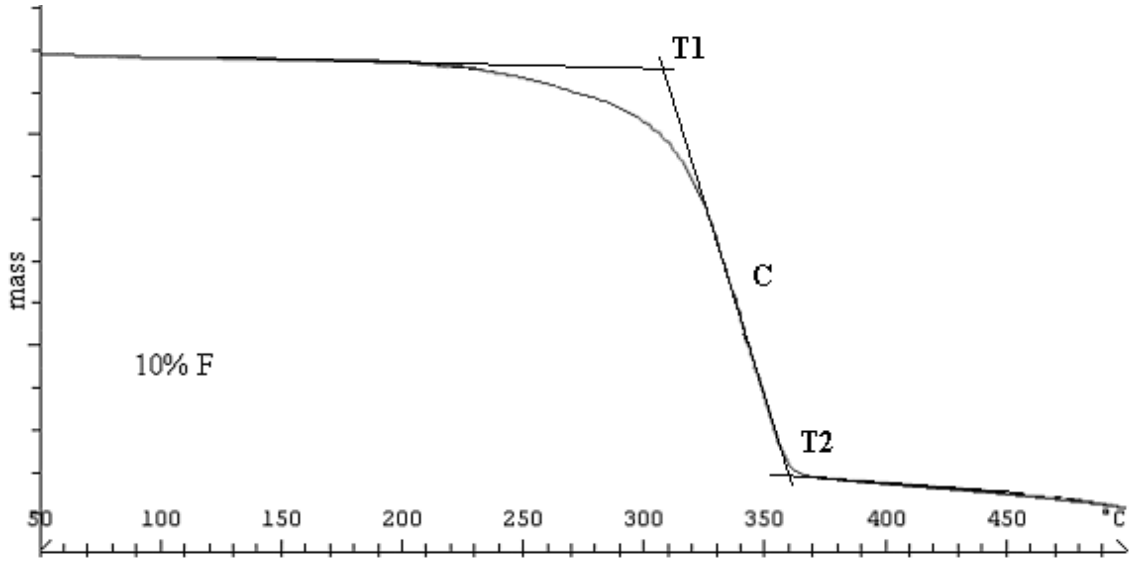

Figure A.10. MDI PPG EDA, 10% fluorinated, unexposed.

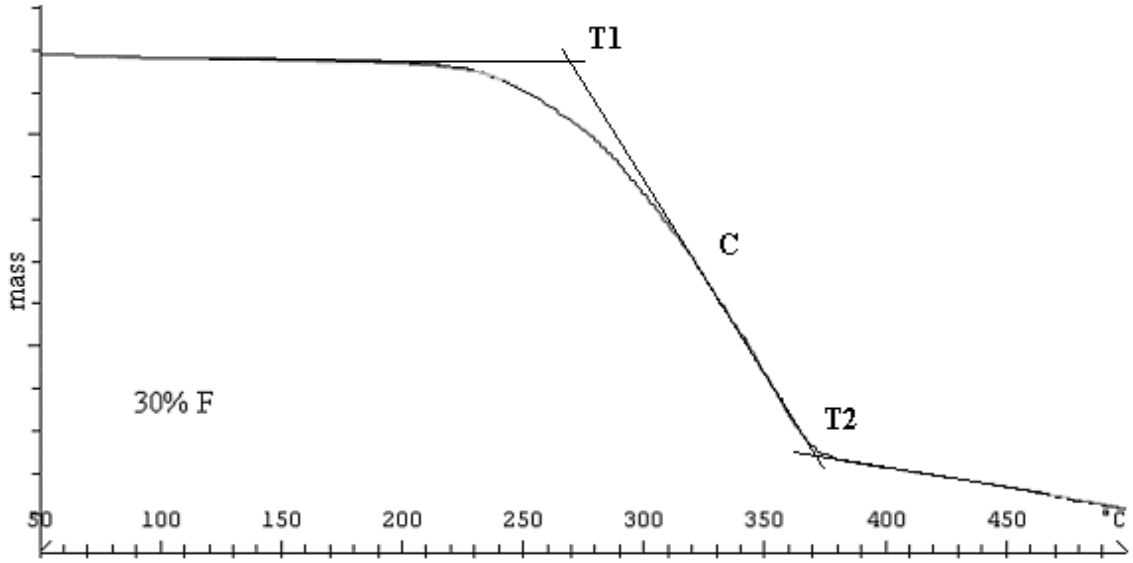

Figure A.11. MDI PPG EDA, 30% fluorinated, unexposed.

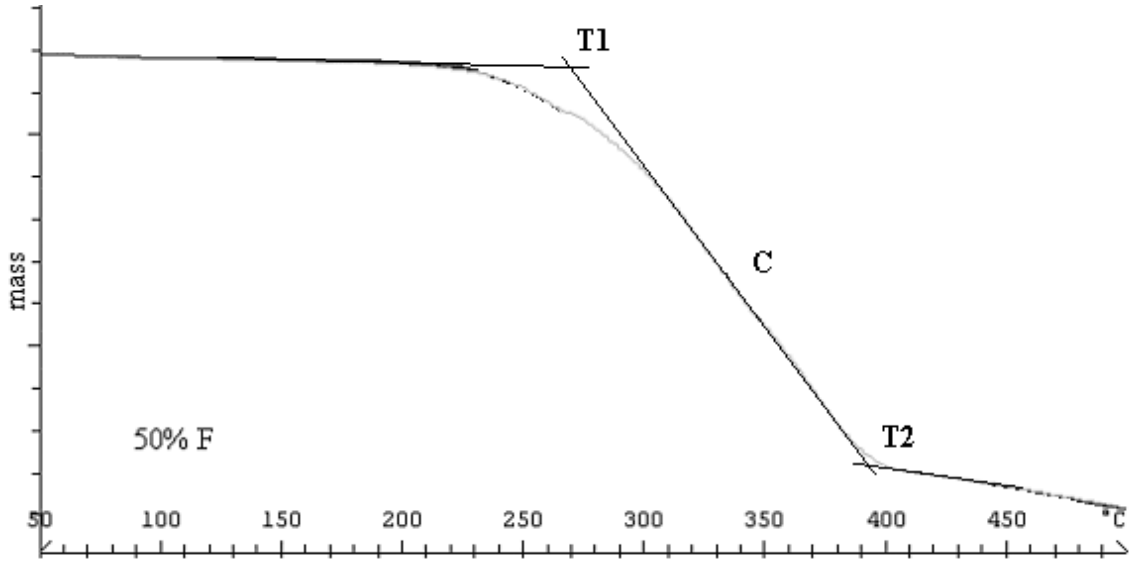

Figure A.12. MDI PPG EDA, 50% fluorinated, unexposed.

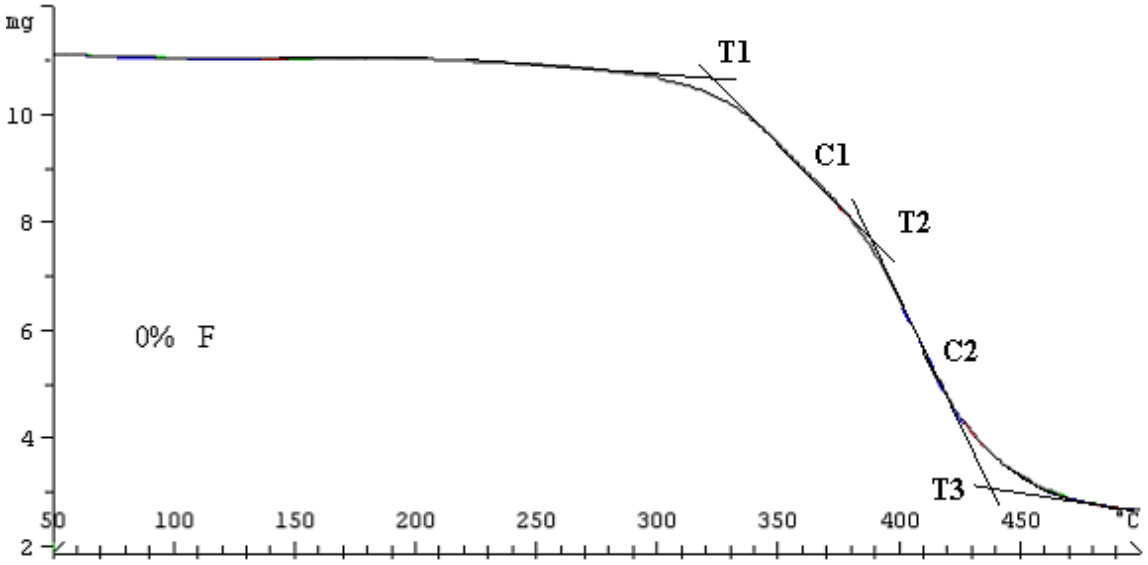

Figure A.13. MDI PTMG EDA, non-fluorinated, unexposed.

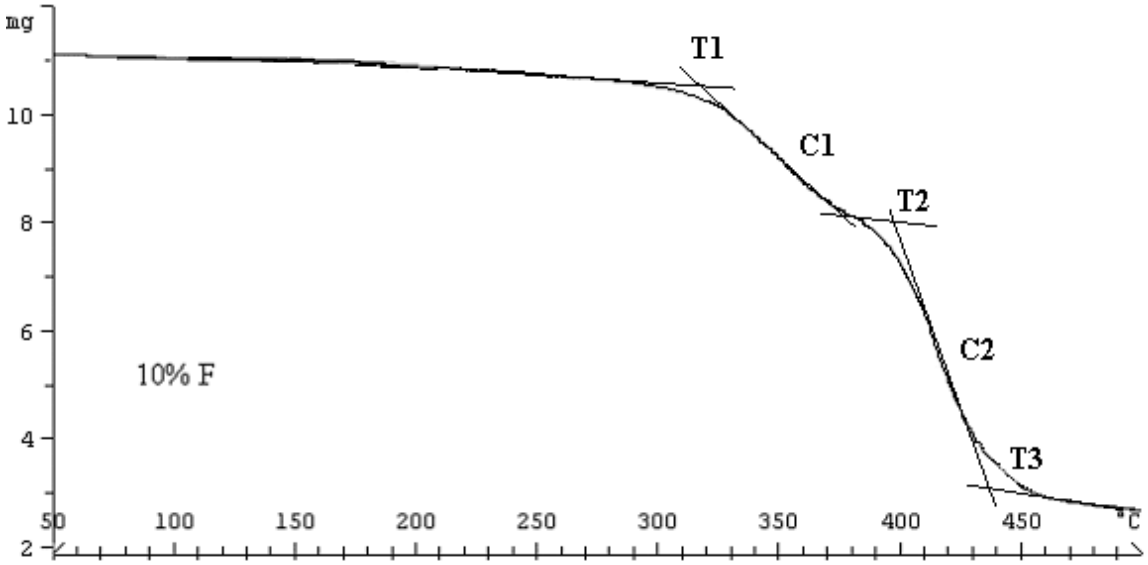

Figure A.14. MDI PTMG EDA, 10% fluorinated, unexposed.

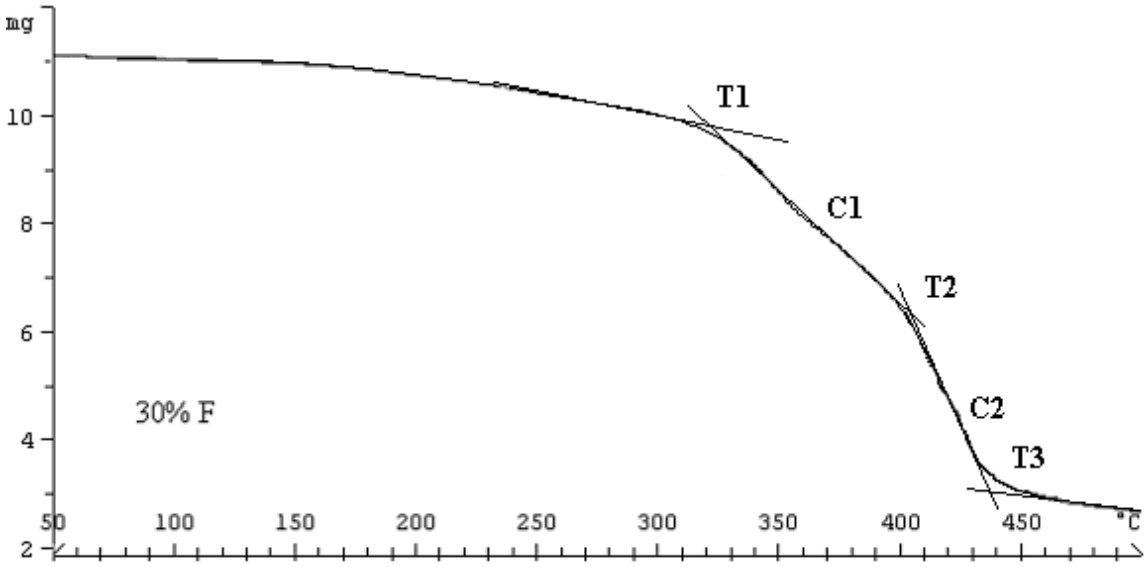

Figure A.15. MDI PTMG EDA, 30% fluorinated, unexposed.

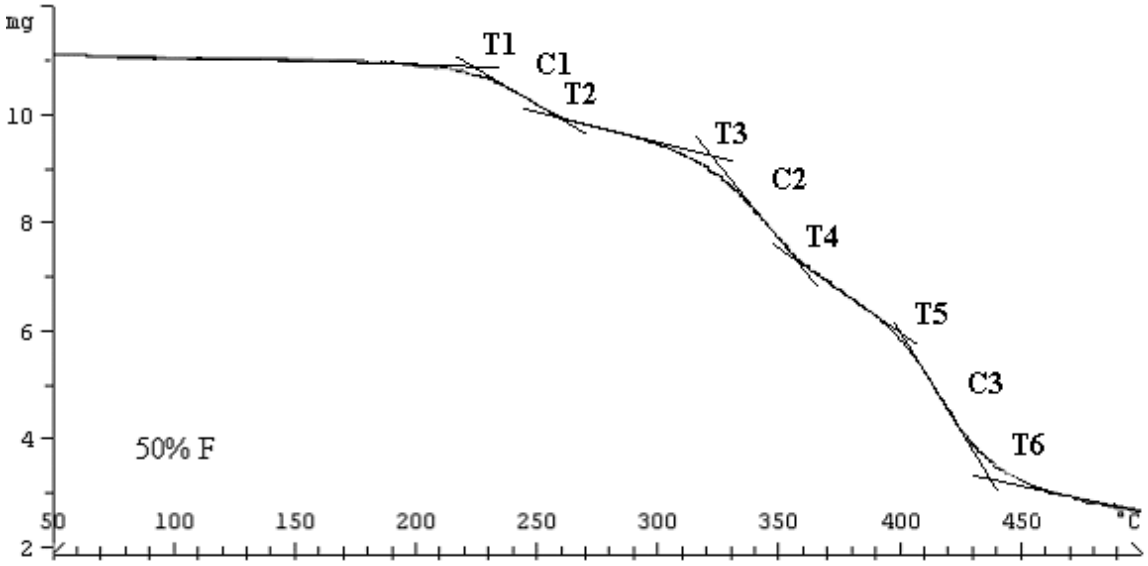

Figure A.16. MDI PTMG EDA, 50% fluorinated, unexposed.

Appendix B: Infrared spectra of all samples

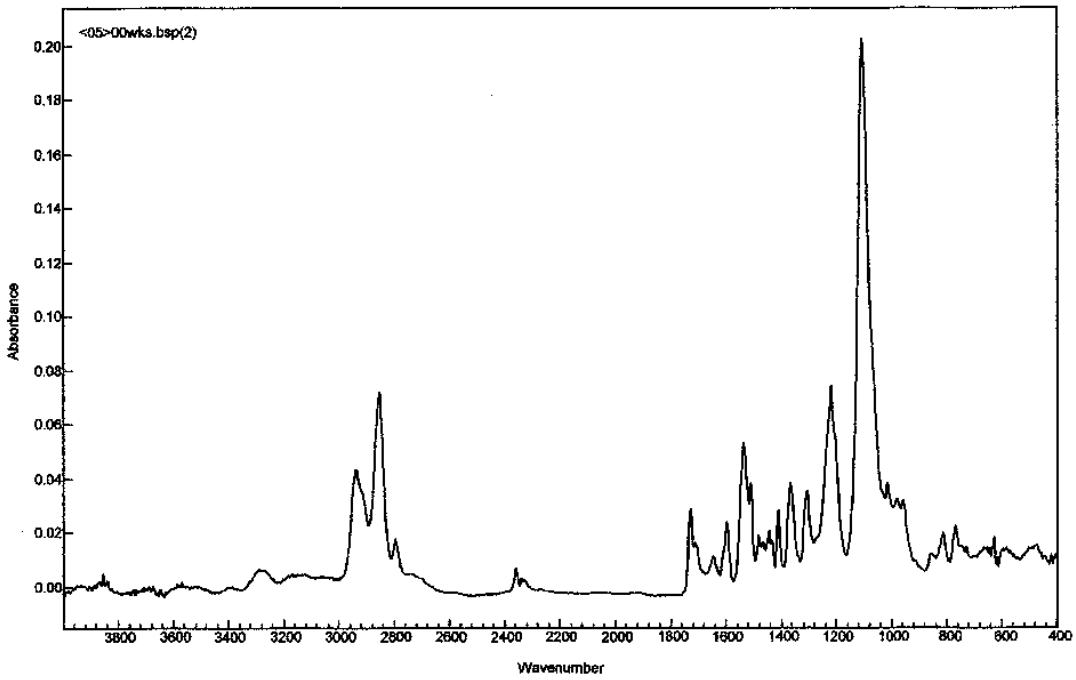

Figure B.1. PTMG based polymer, 0% fluorinated, unexposed.

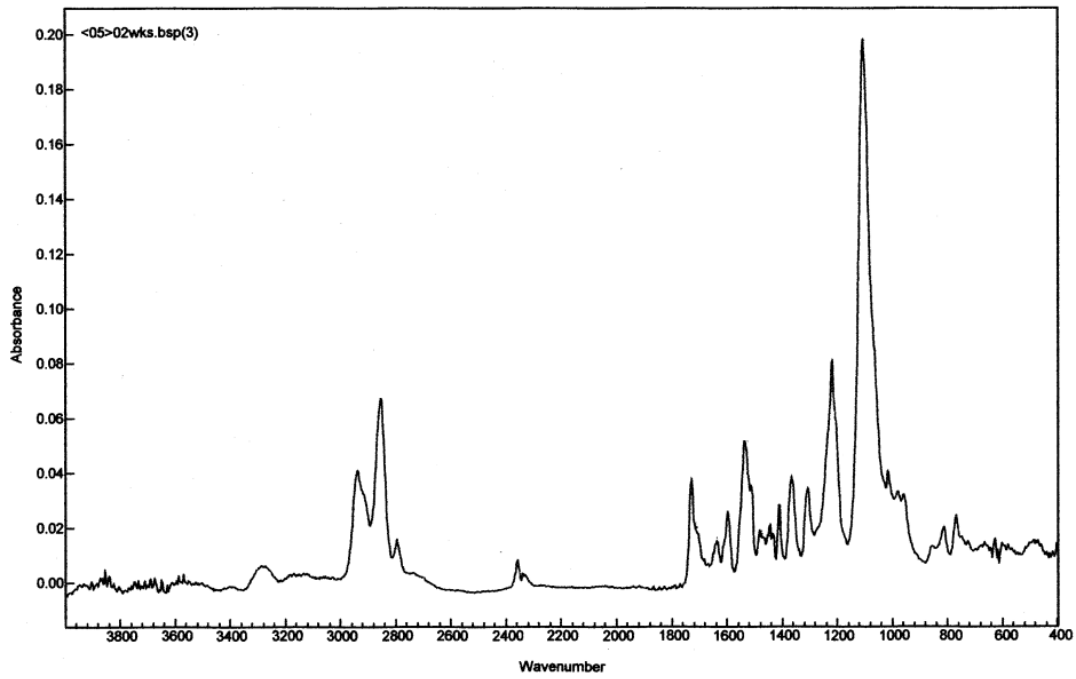

Figure B.2. PTMG based polymer, 0% fluorinated, exposed for 02 weeks.

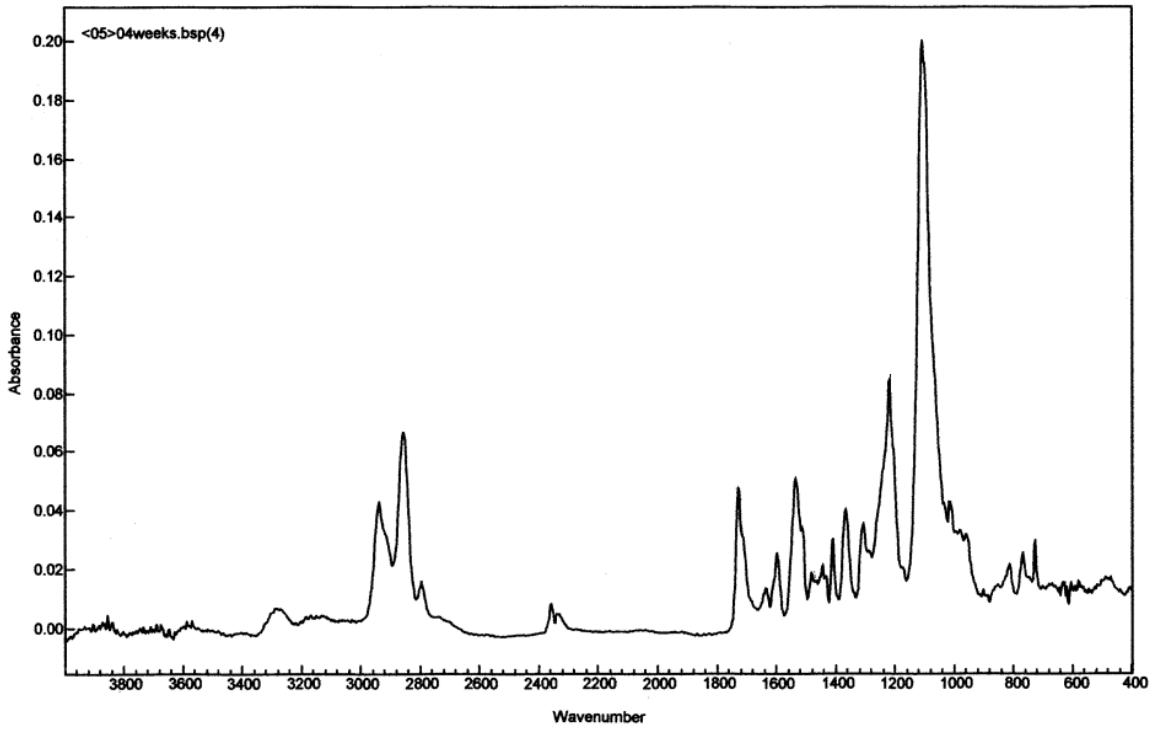

Figure B.3. PTMG based polymer, 0% fluorinated, exposed for 04 weeks.

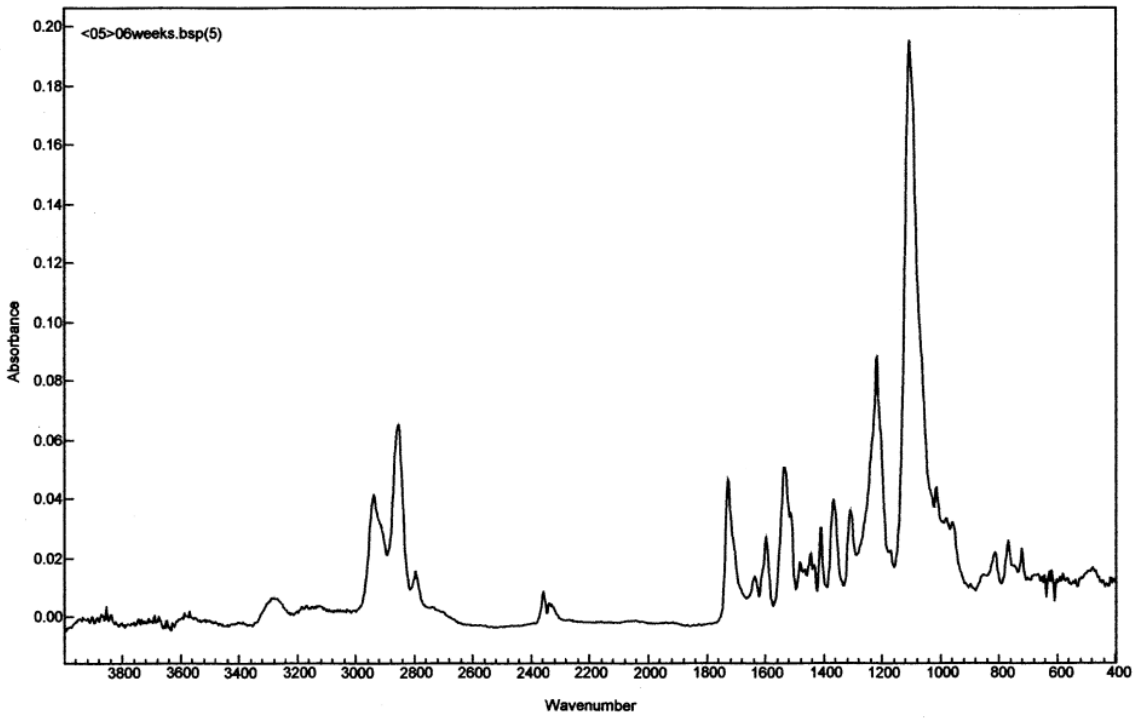

Figure B.4. PTMG based polymer, 0% fluorinated, exposed for 06 weeks.

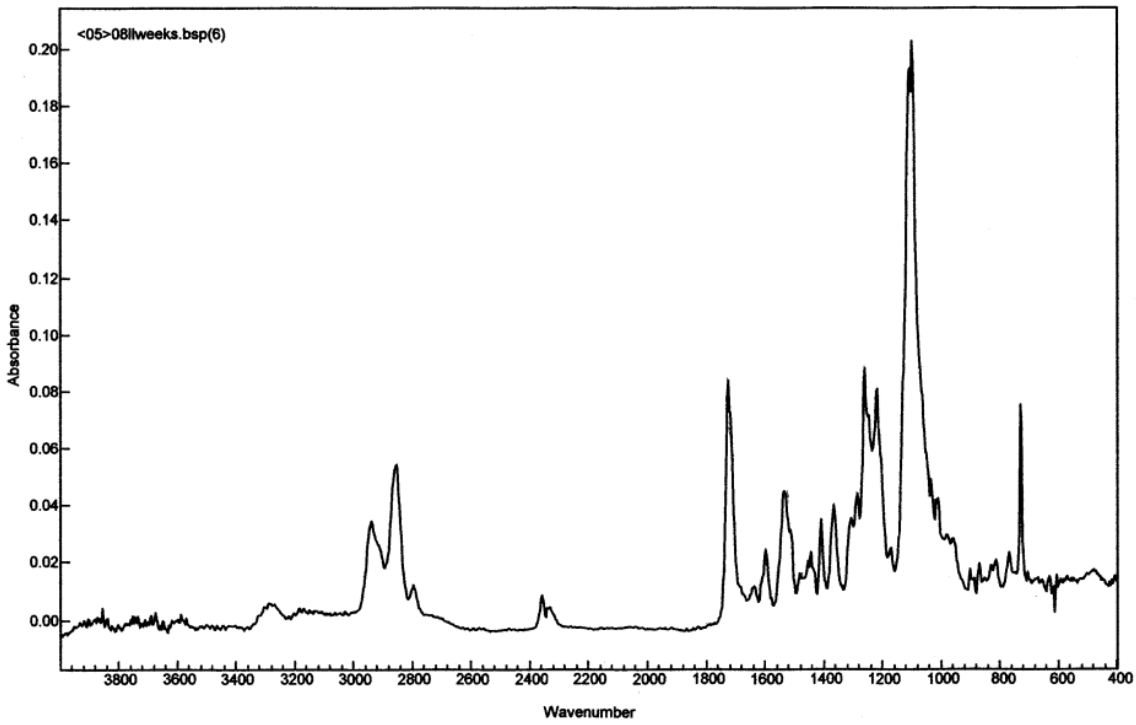

Figure B.5. PTMG based polymer, 0% fluorinated, exposed for 08 weeks.

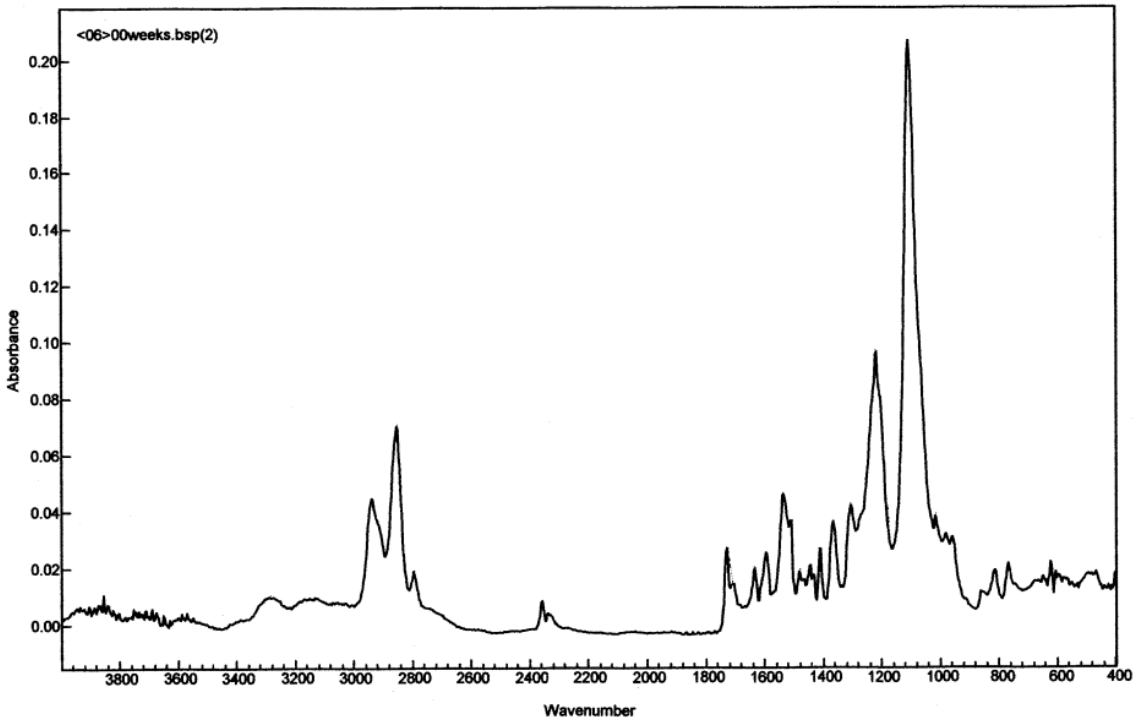

Figure B.6. PTMG based polymer, 10% fluorinated, unexposed.

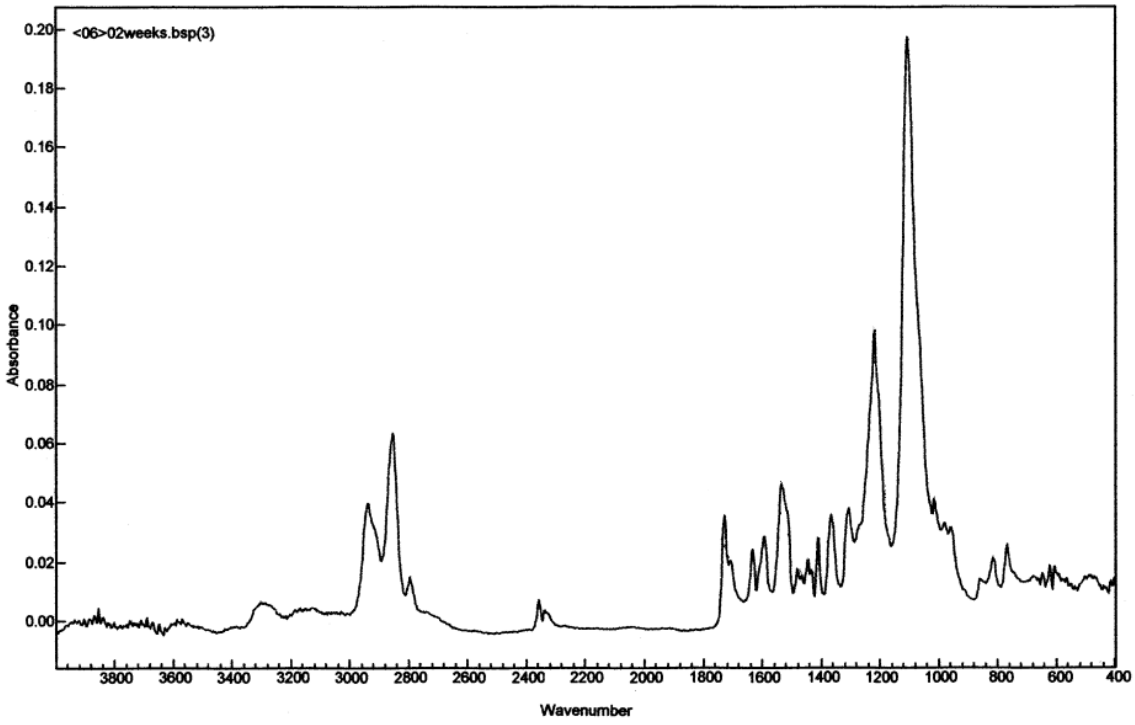

Figure B.7. PTMG based polymer, 10% fluorinated, exposed for 02 weeks.

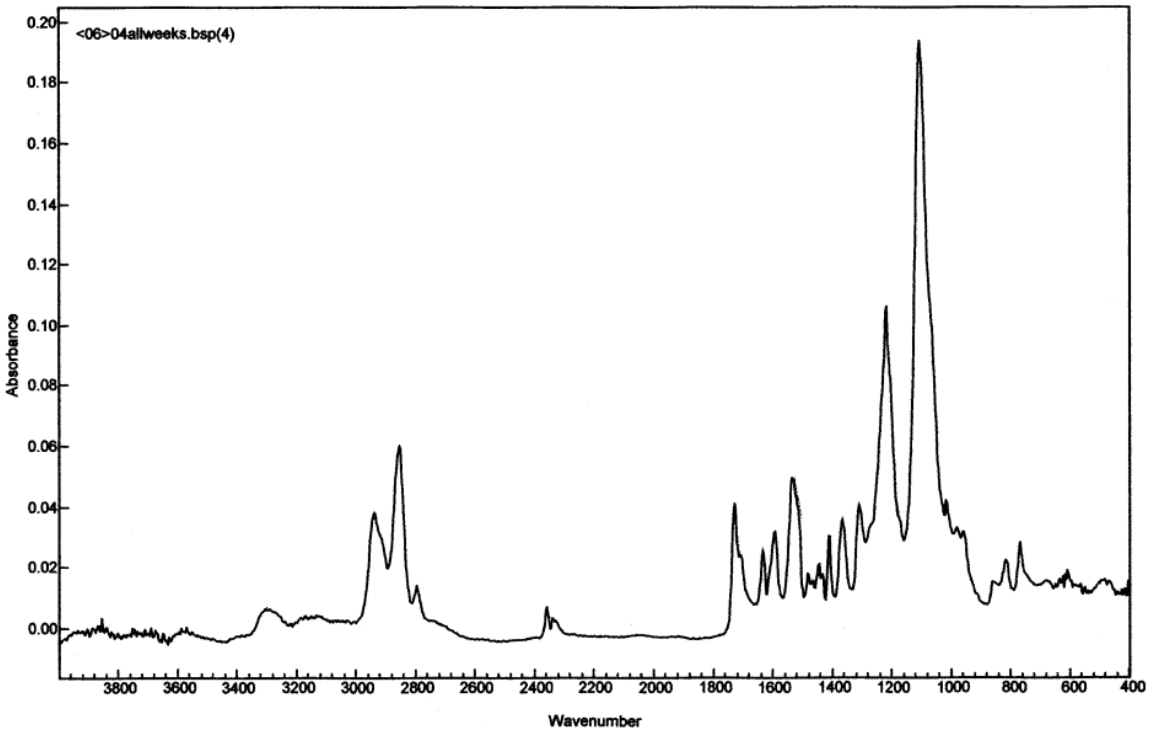

Figure B.8. PTMG based polymer, 10% fluorinated, exposed for 04 weeks.

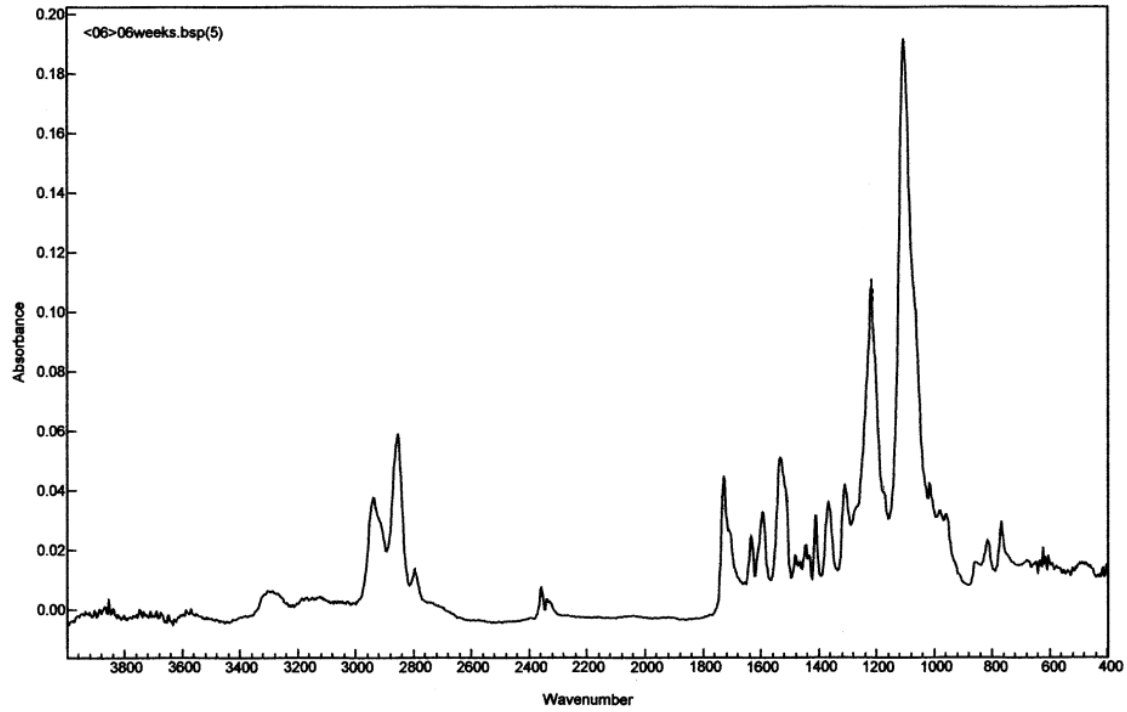

Figure B.9. PTMG based polymer, 10% fluorinated, exposed for 06 weeks.

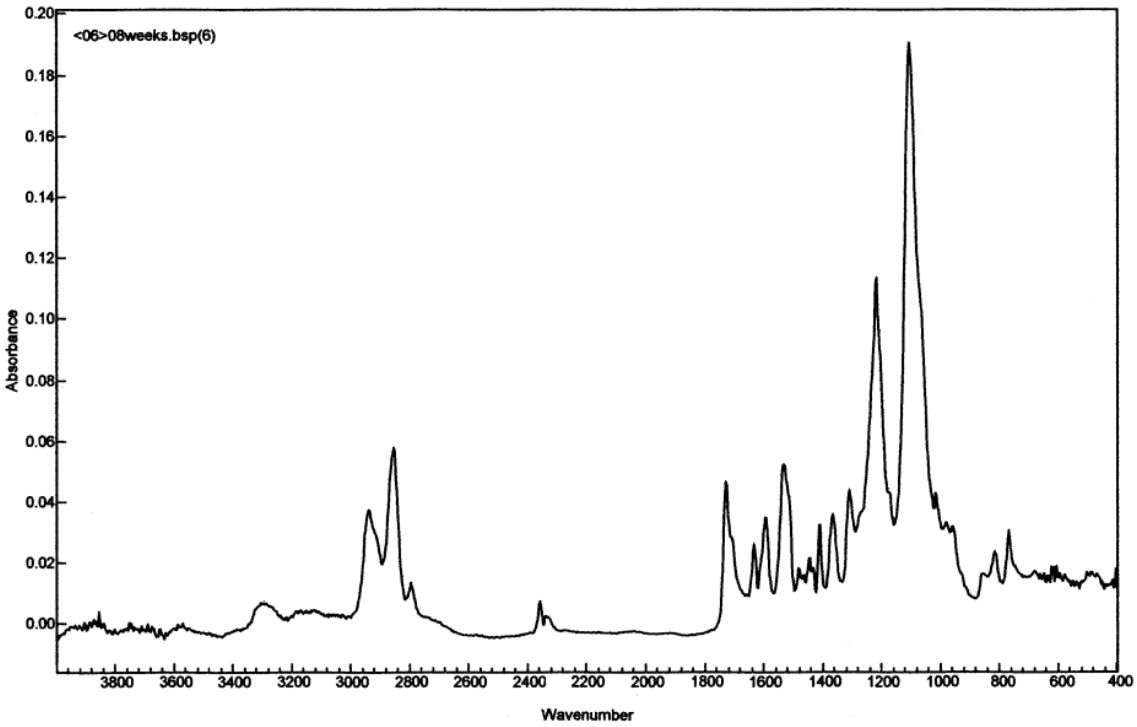

Figure B.10. PTMG based polymer, 10% fluorinated, exposed for 08 weeks.

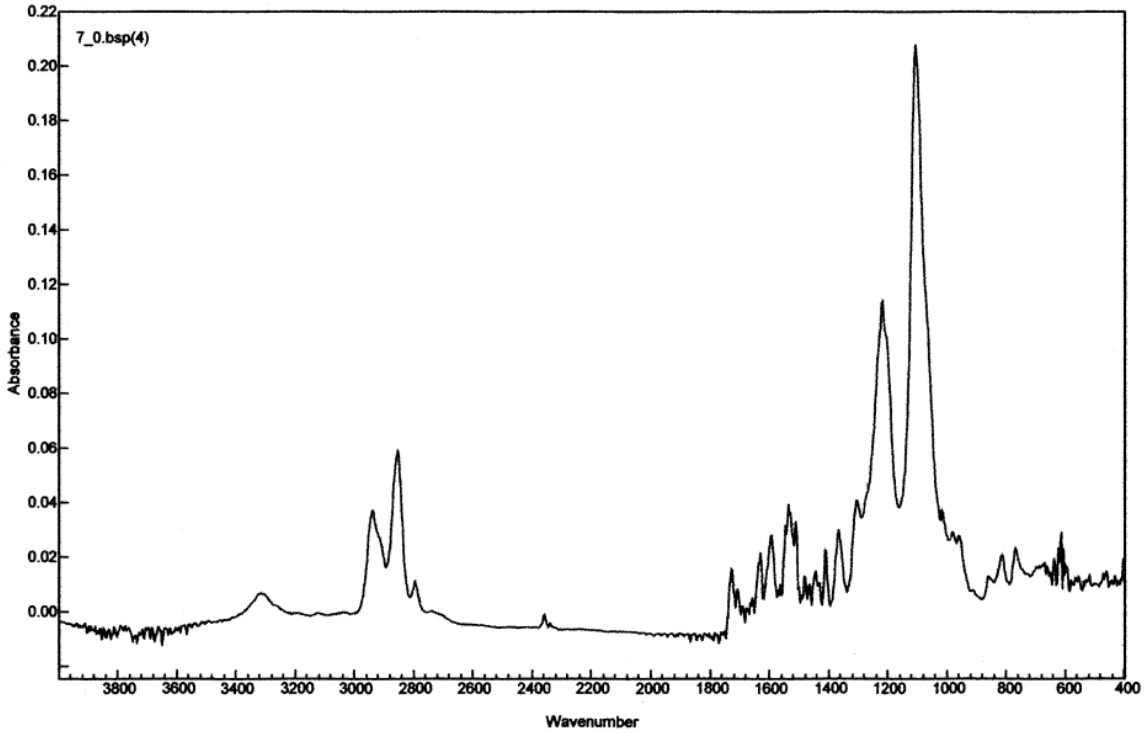

Figure B.11. PTMG based polymer, 30% fluorinated, unexposed.

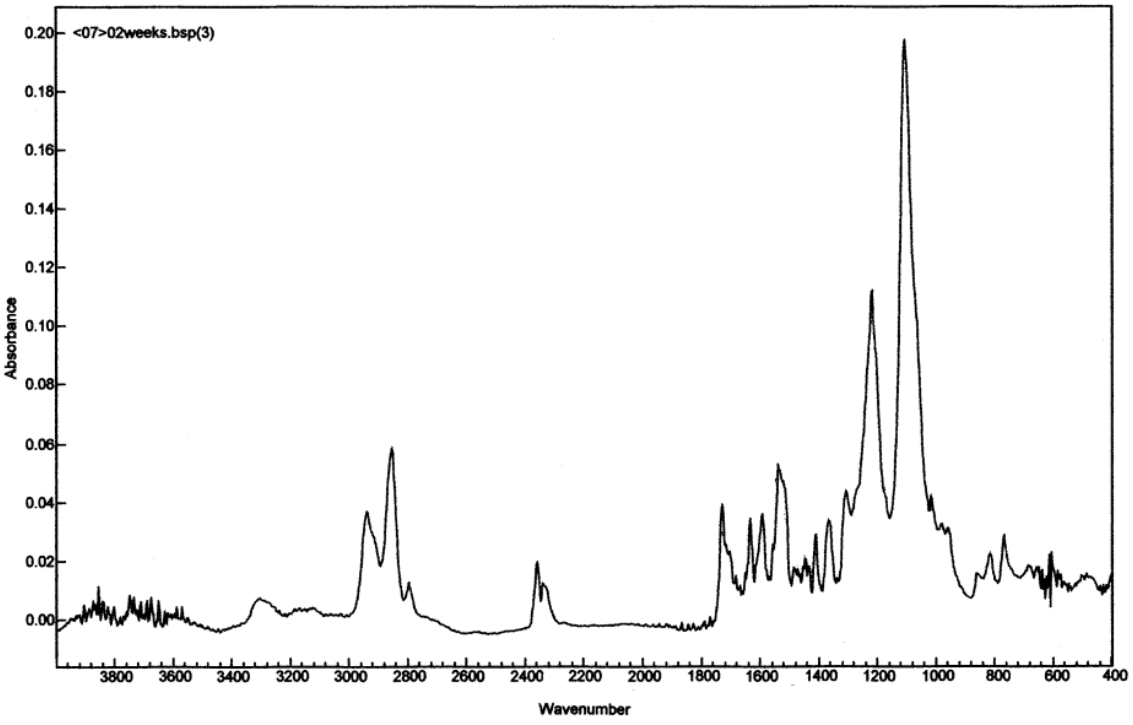

Figure B.12. PTMG based polymer, 30% fluorinated, exposed for 02 weeks.

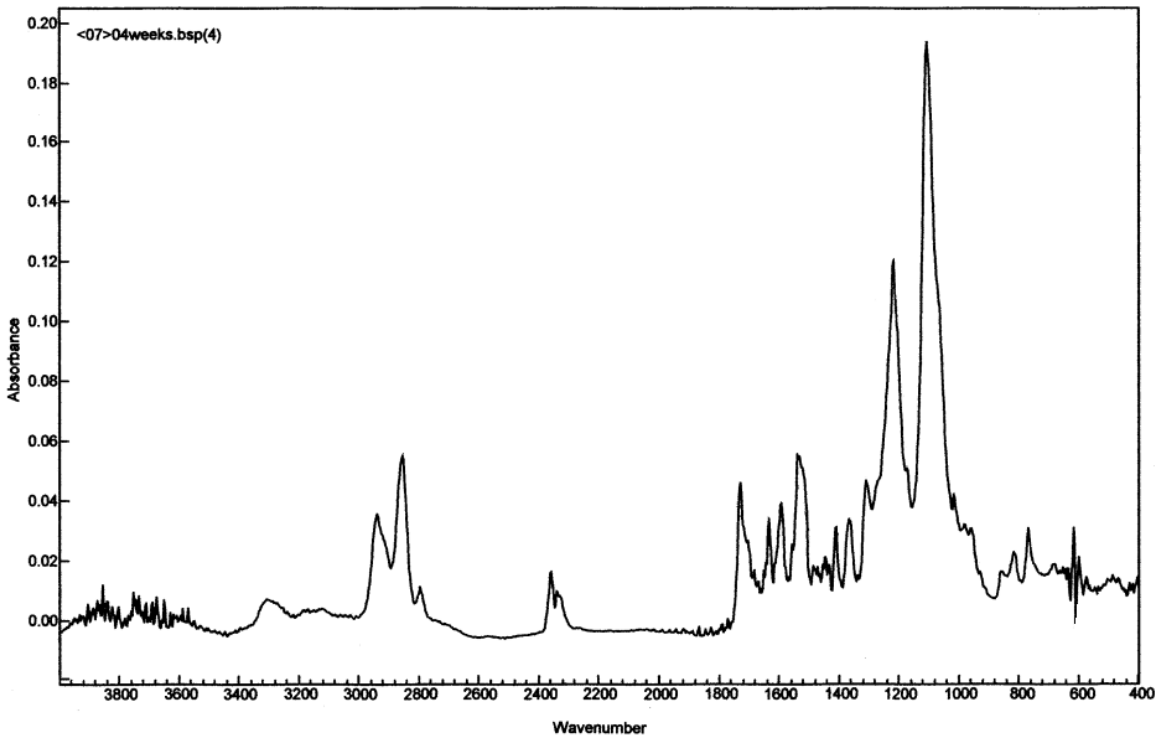

Figure B.13. PTMG based polymer, 30% fluorinated, exposed for 04 weeks.

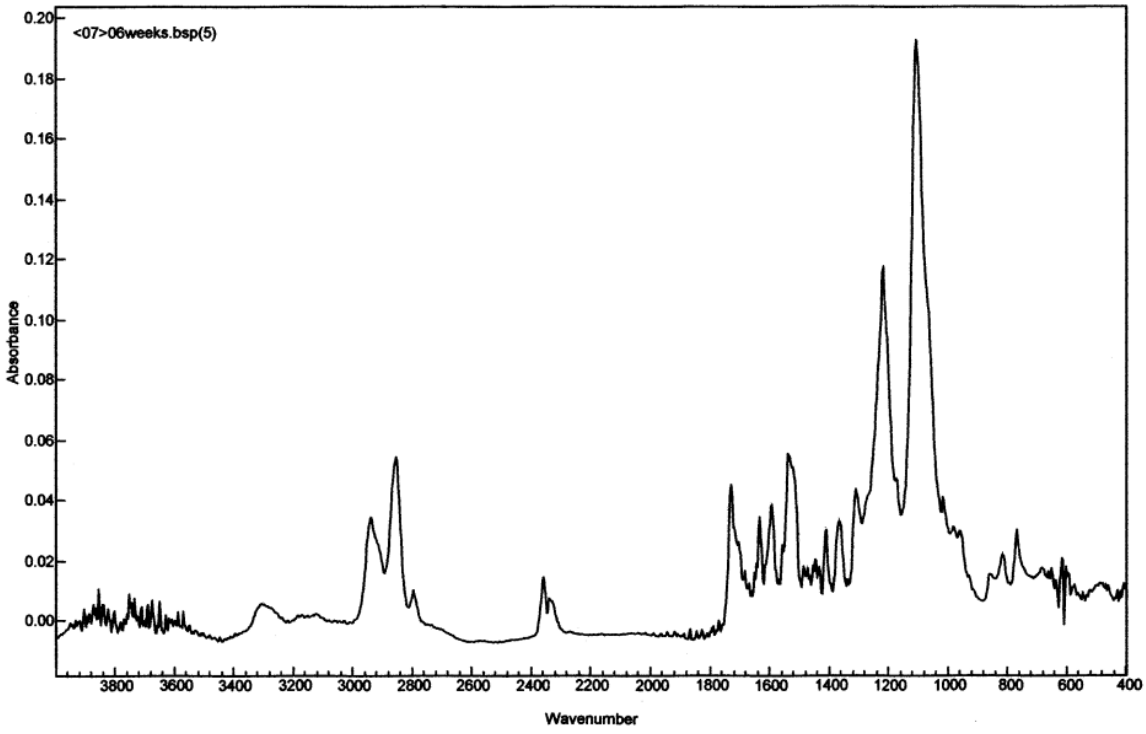

Figure B.14. PTMG based polymer, 30% fluorinated, exposed for 06 weeks.

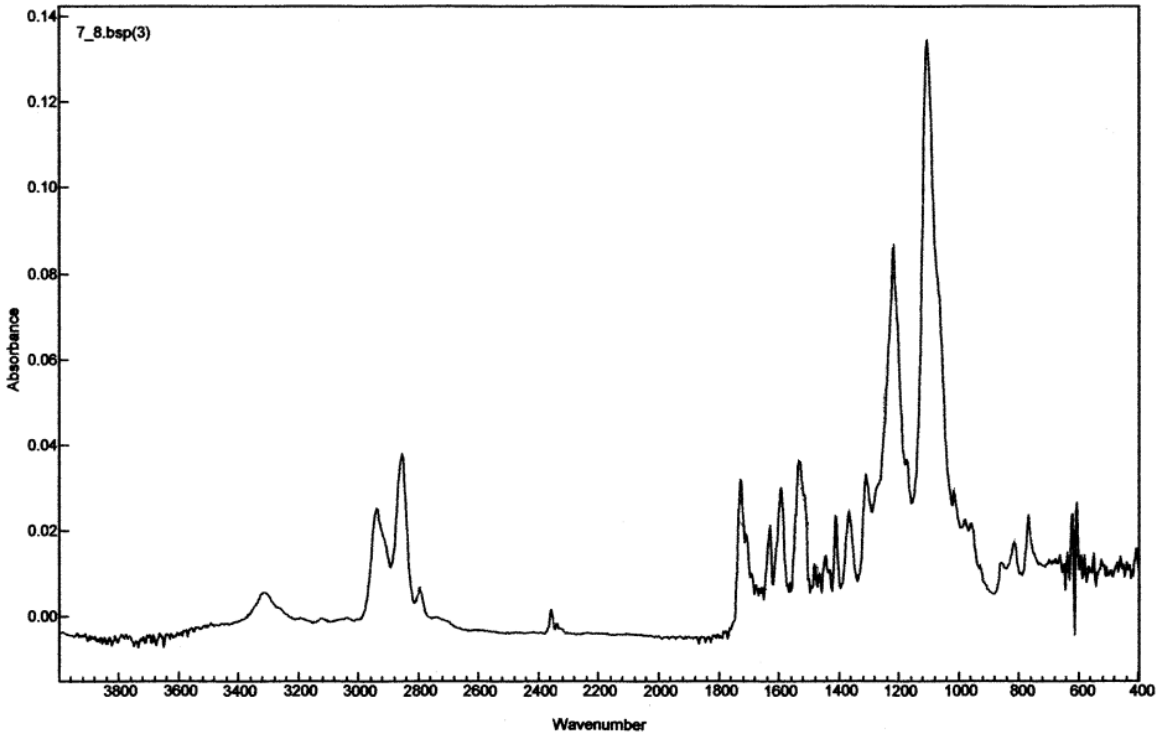

Figure B.15. PTMG based polymer, 30% fluorinated, exposed for 08 weeks.

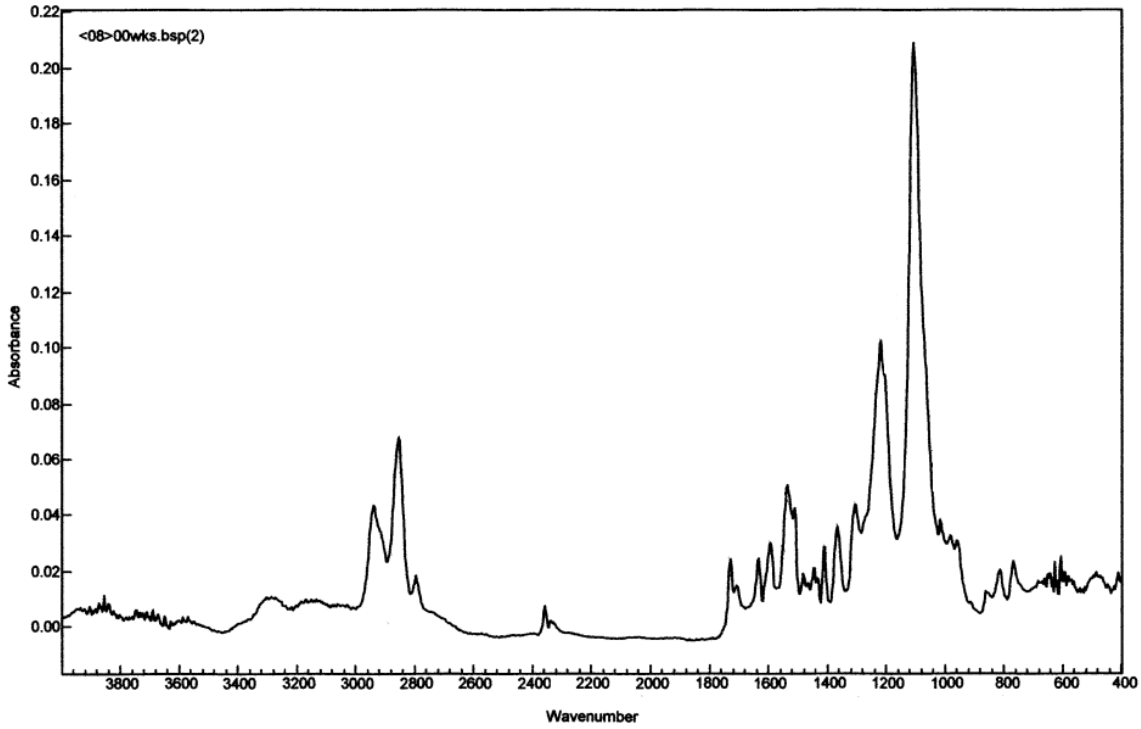

Figure B.16. PTMG based polymer, 50% fluorinated, unexposed.

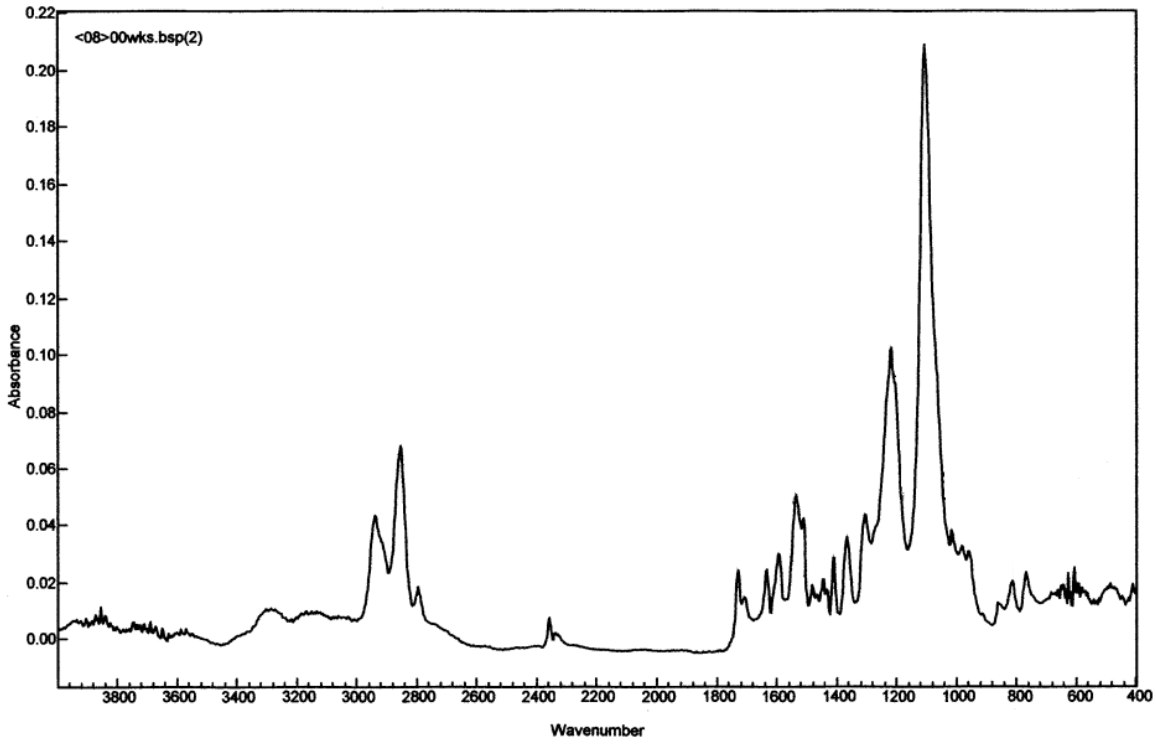

Figure B.17. PTMG based polymer, 50% fluorinated, exposed for 02 weeks.

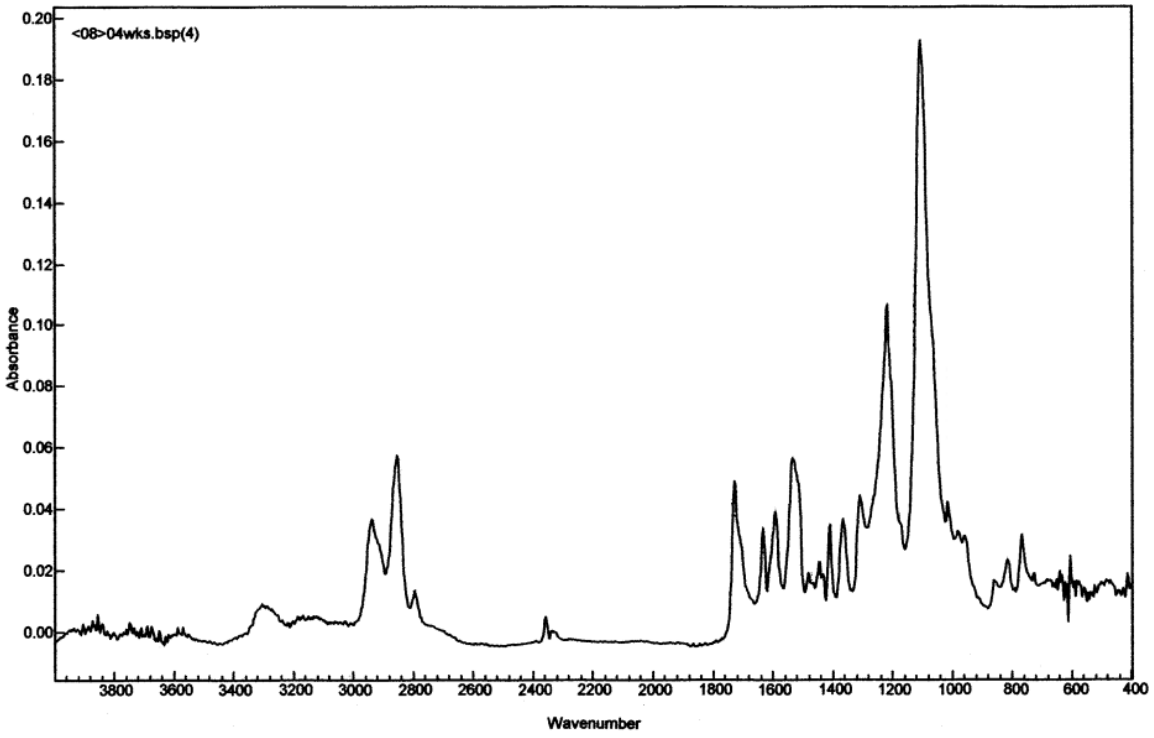

Figure B.18. PTMG based polymer, 50% fluorinated, exposed for 04 weeks.

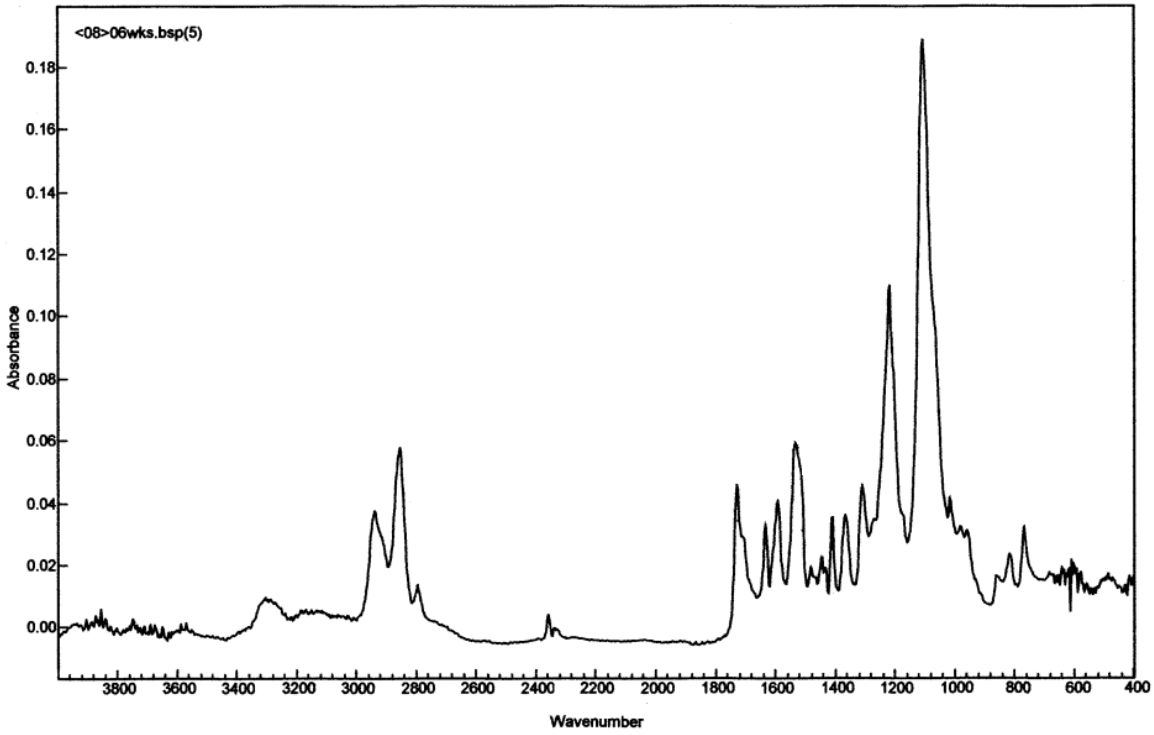

Figure B.19. PTMG based polymer, 50% fluorinated, exposed for 06 weeks.

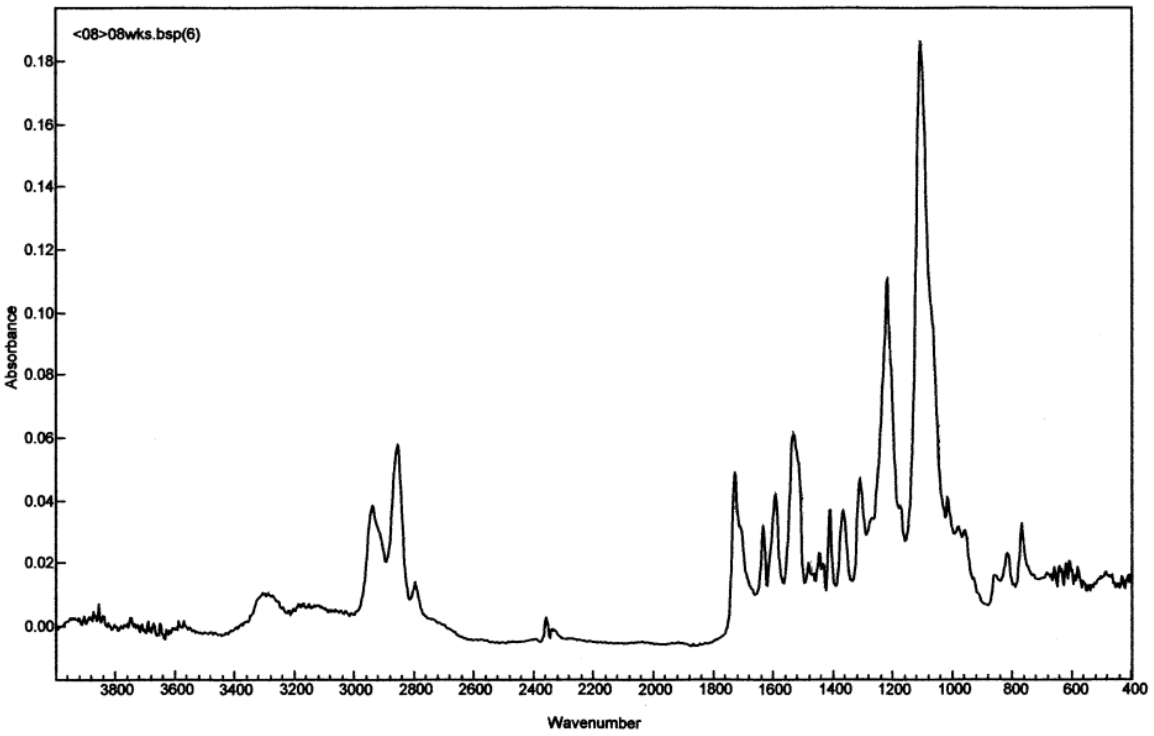

Figure B.20. PTMG based polymer, 50% fluorinated, exposed for 08 weeks.

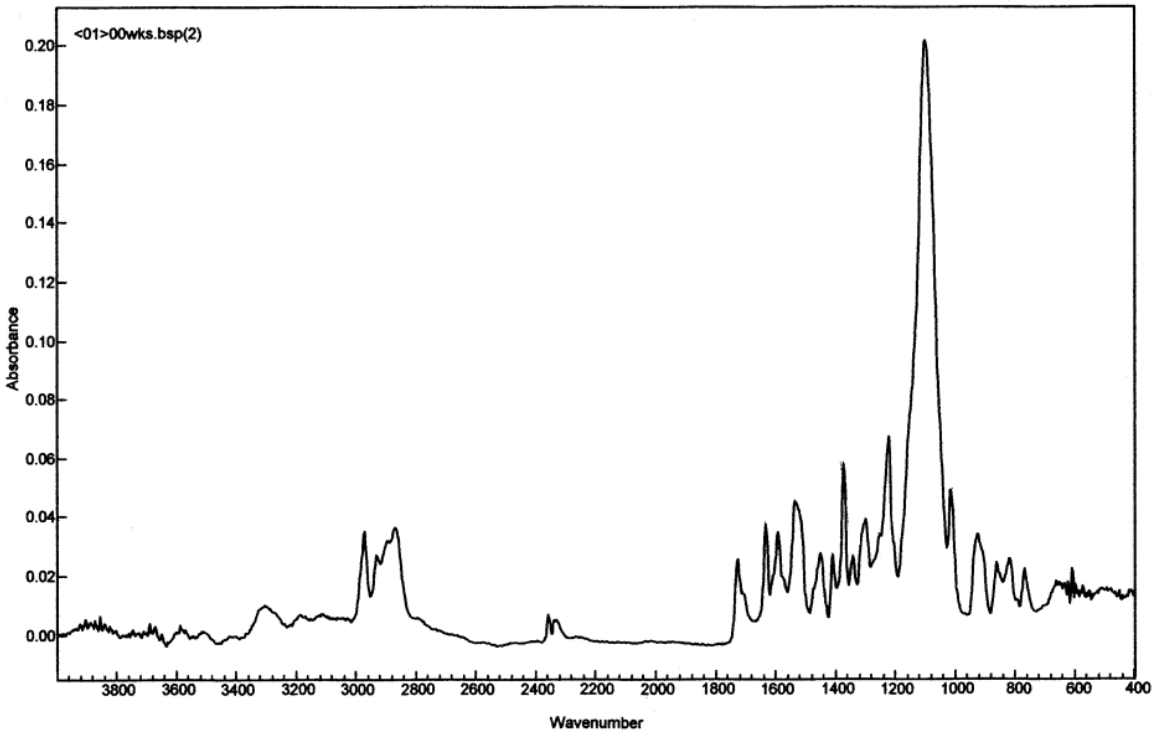

Figure B.21. PPG based polymer, 0% fluorinated, unexposed.

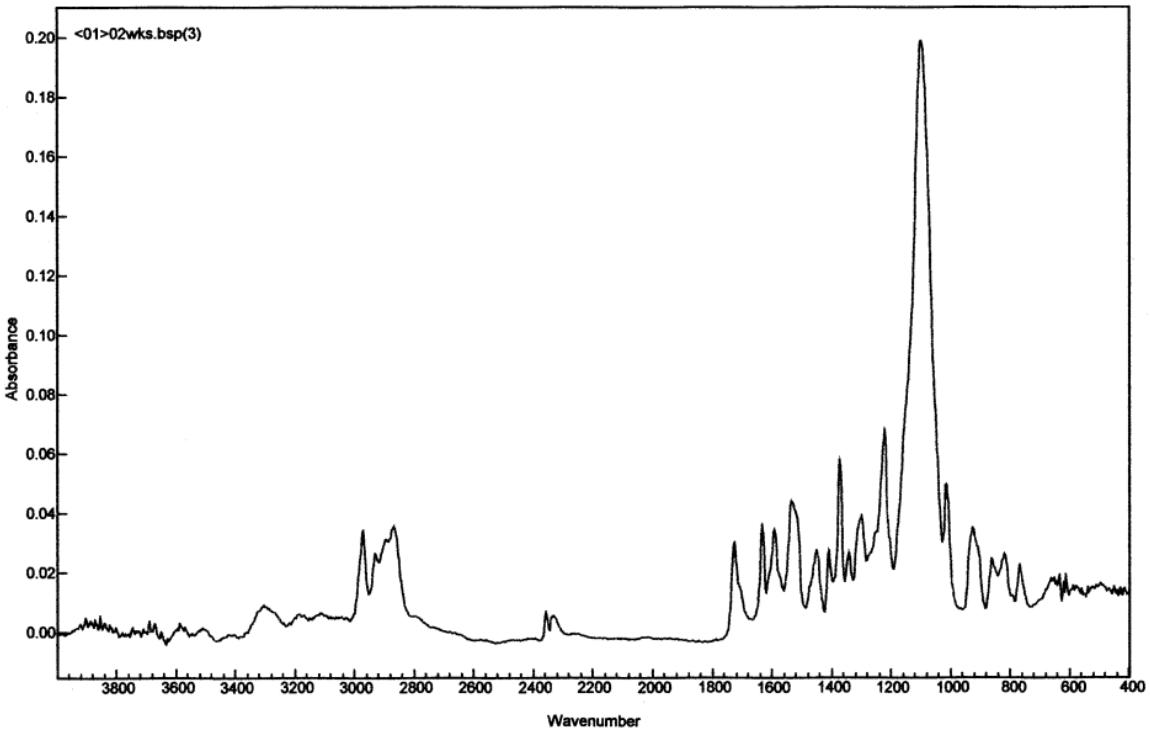

Figure B.22. PPG based polymer, 0% fluorinated, exposed for 02 weeks.

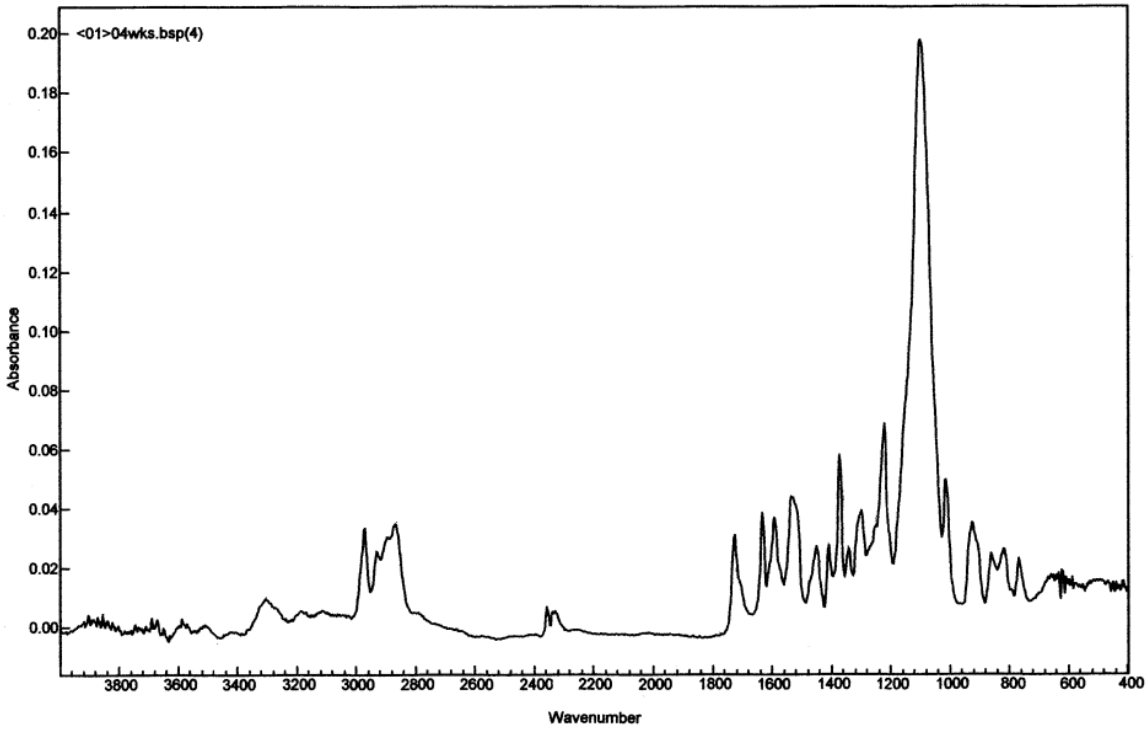

Figure B.23. PPG based polymer, 0% fluorinated, exposed for 04 weeks.

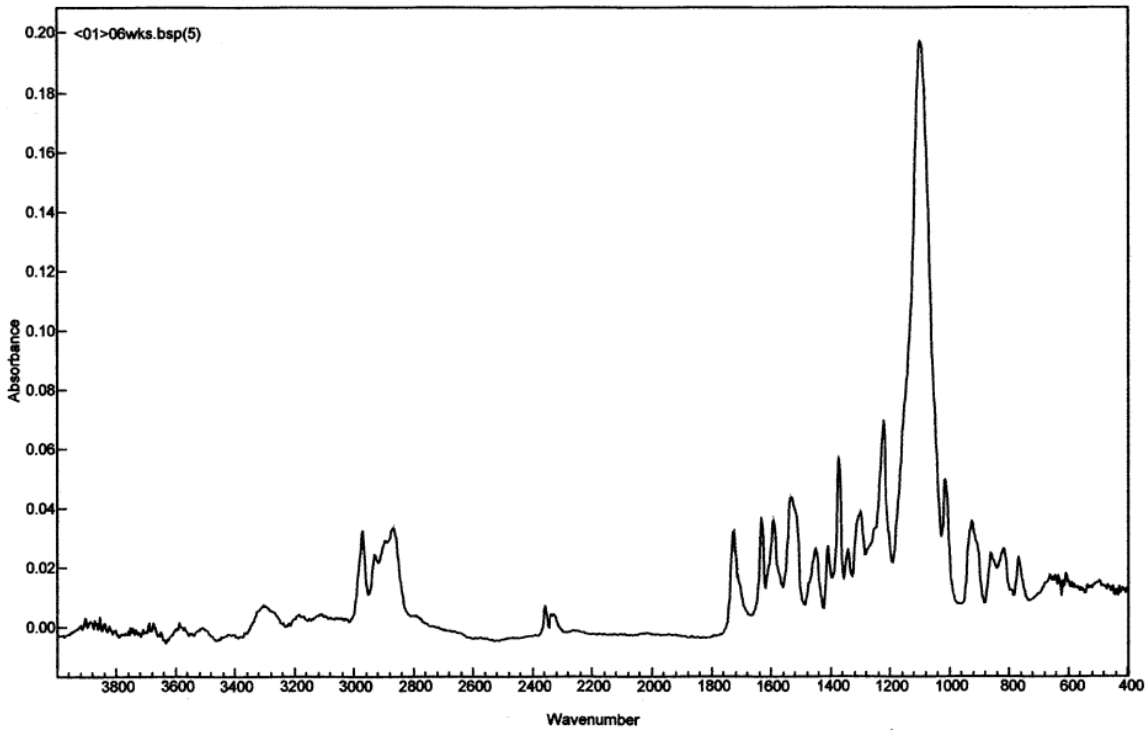

Figure B.24. PPG based polymer, 0% fluorinated, exposed for 06 weeks.

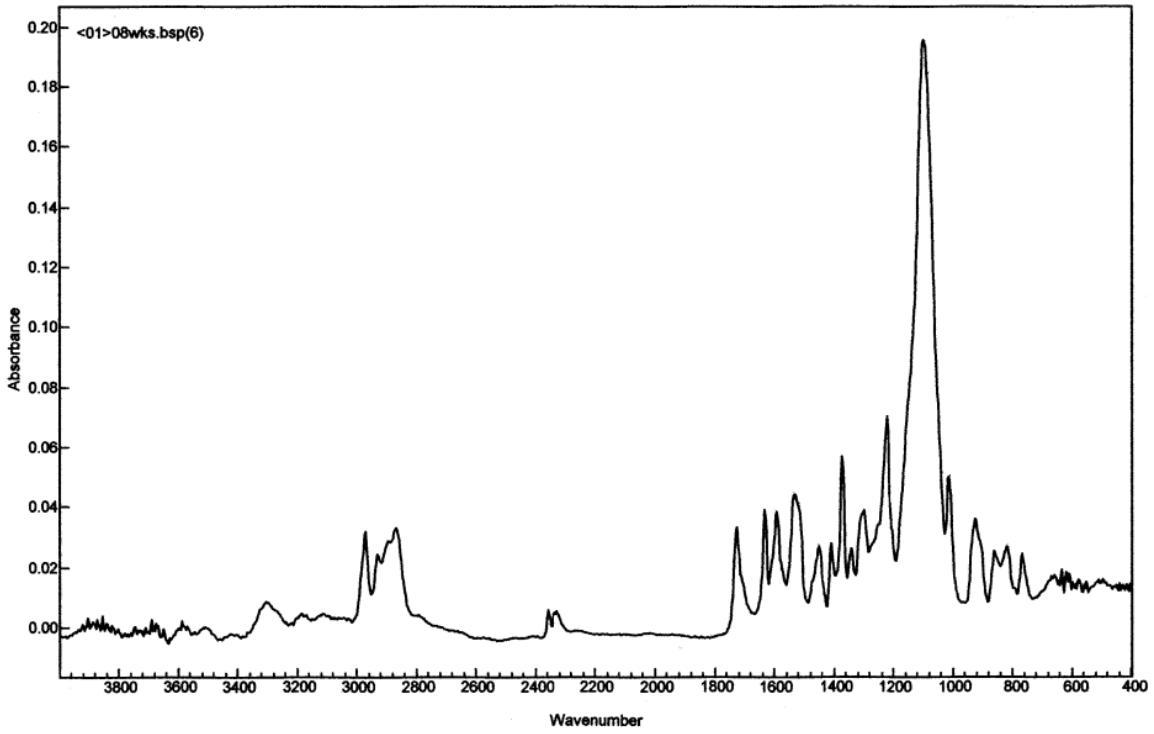

Figure B.25. PPG based polymer, 0% fluorinated, exposed for 08 weeks.

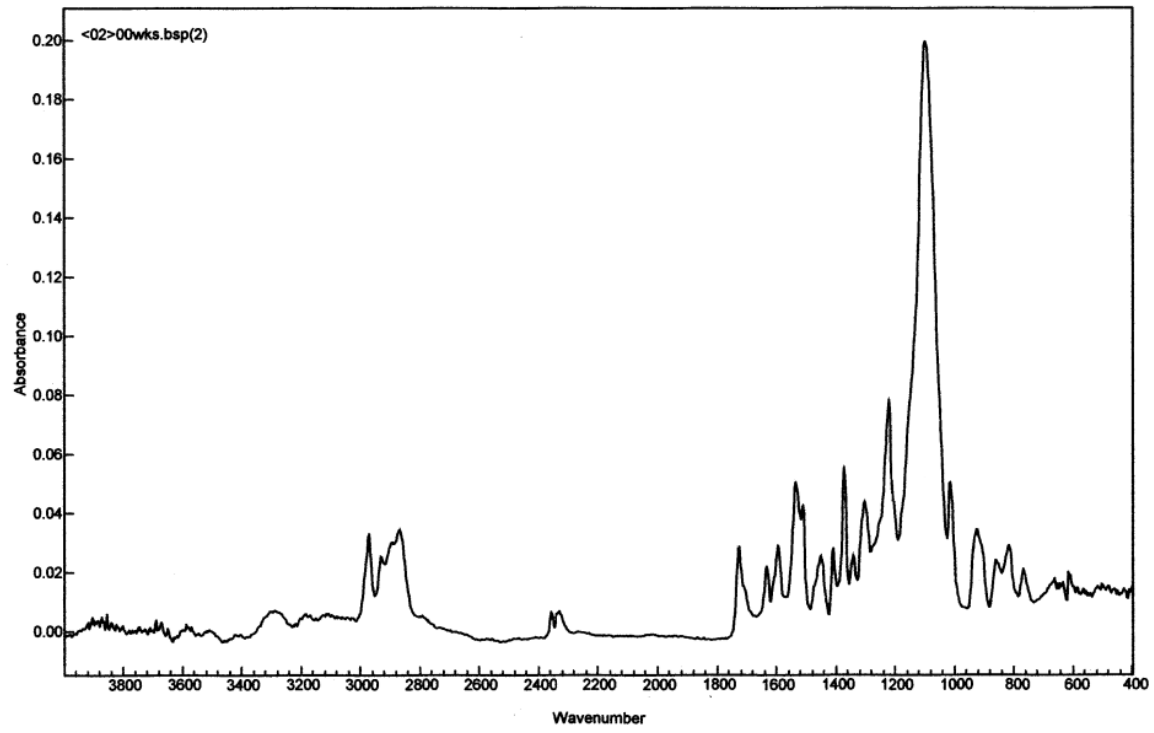

Figure B.26. PPG based polymer, 10% fluorinated, unexposed.

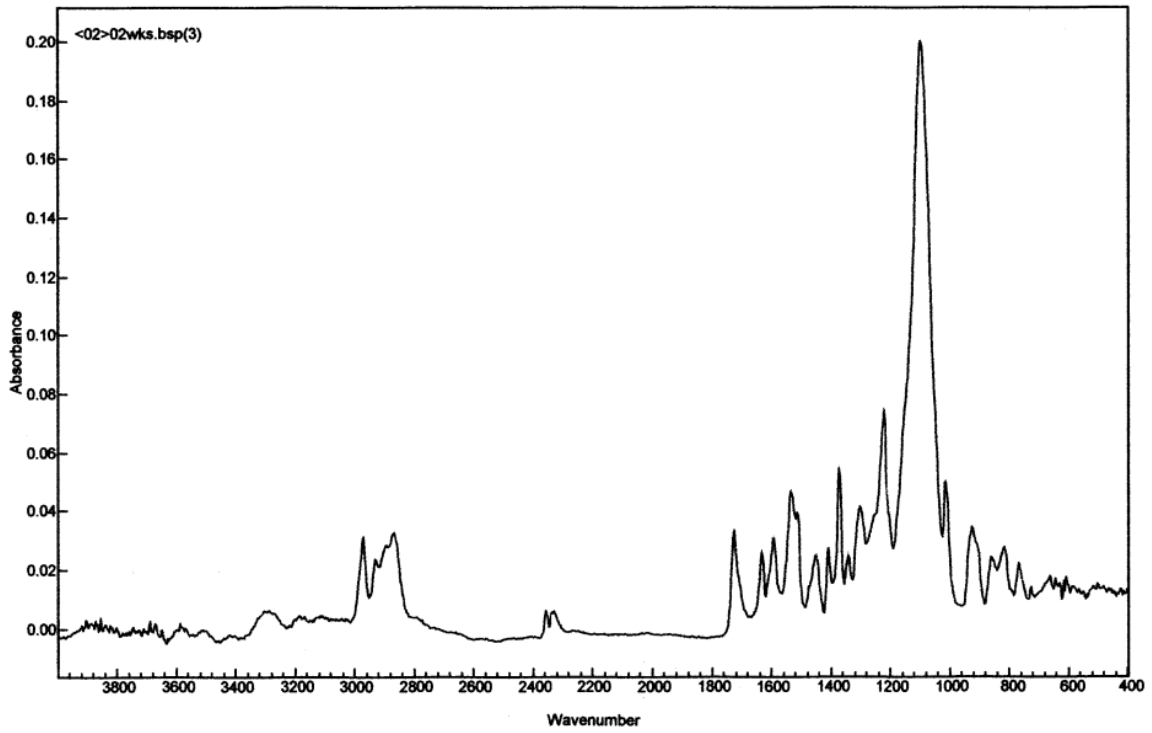

Figure B.27. PPG based polymer, 10% fluorinated, exposed for 02 weeks.

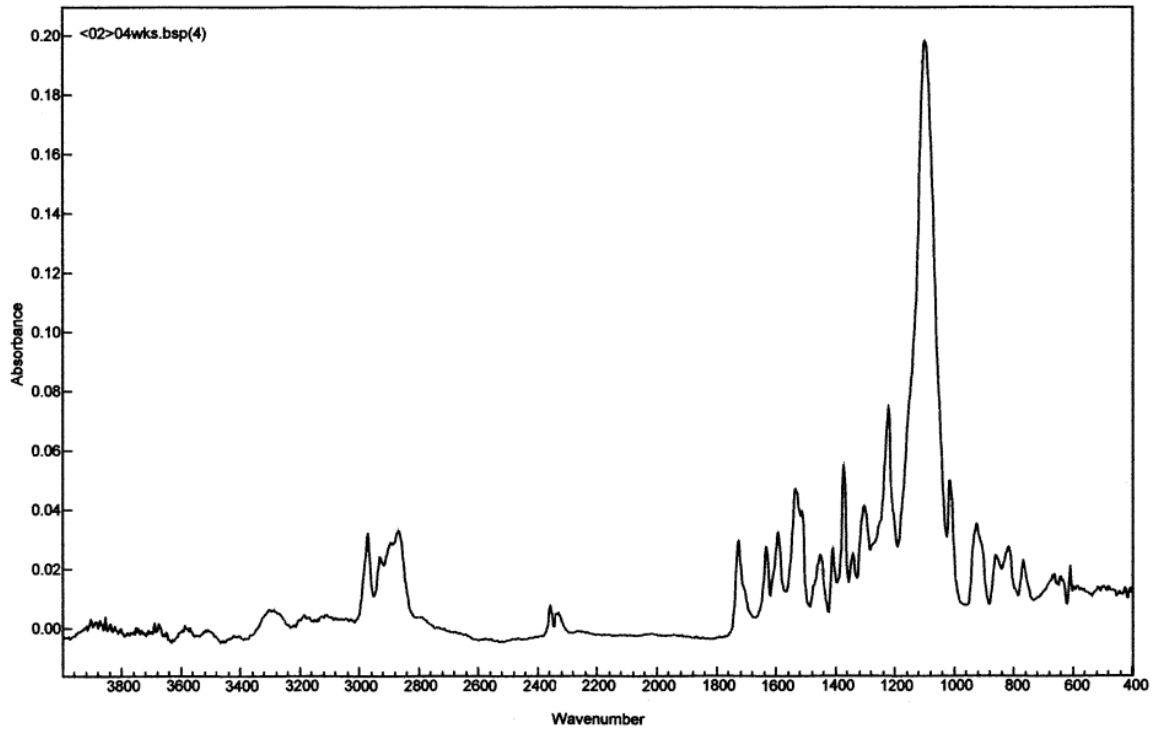

Figure B.28. PPG based polymer, 10% fluorinated, exposed for 04 weeks.

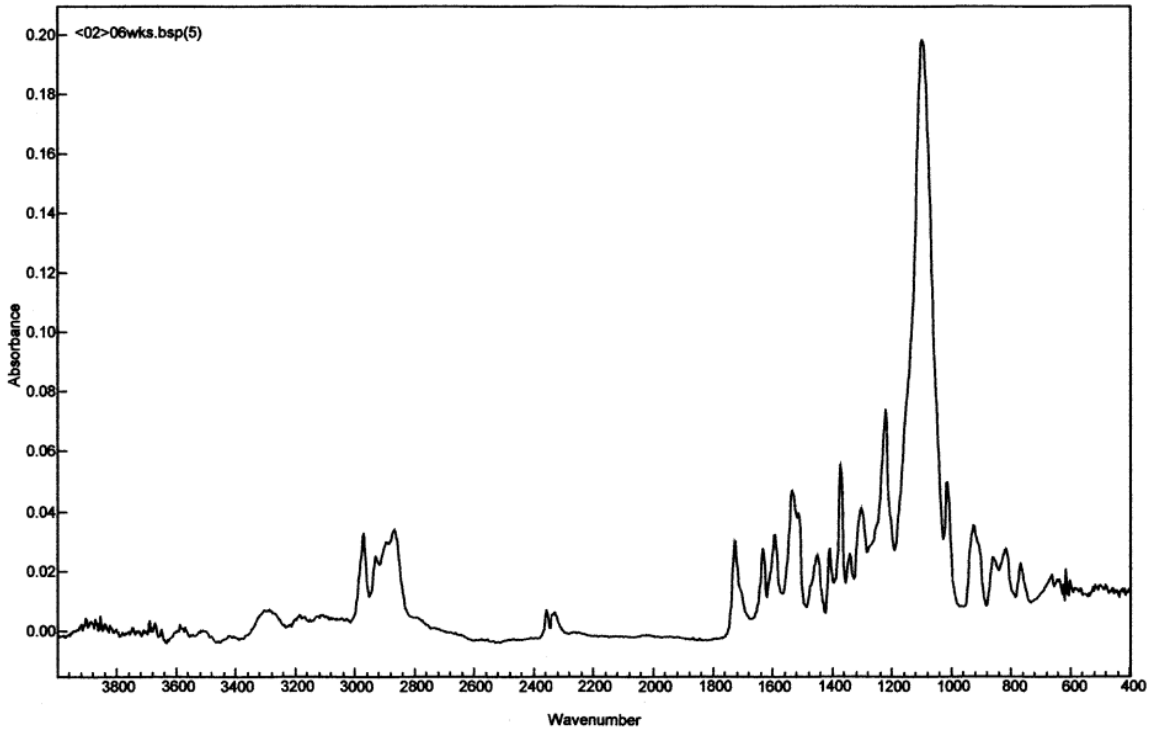

Figure B.29. PPG based polymer, 10% fluorinated, exposed for 06 weeks.

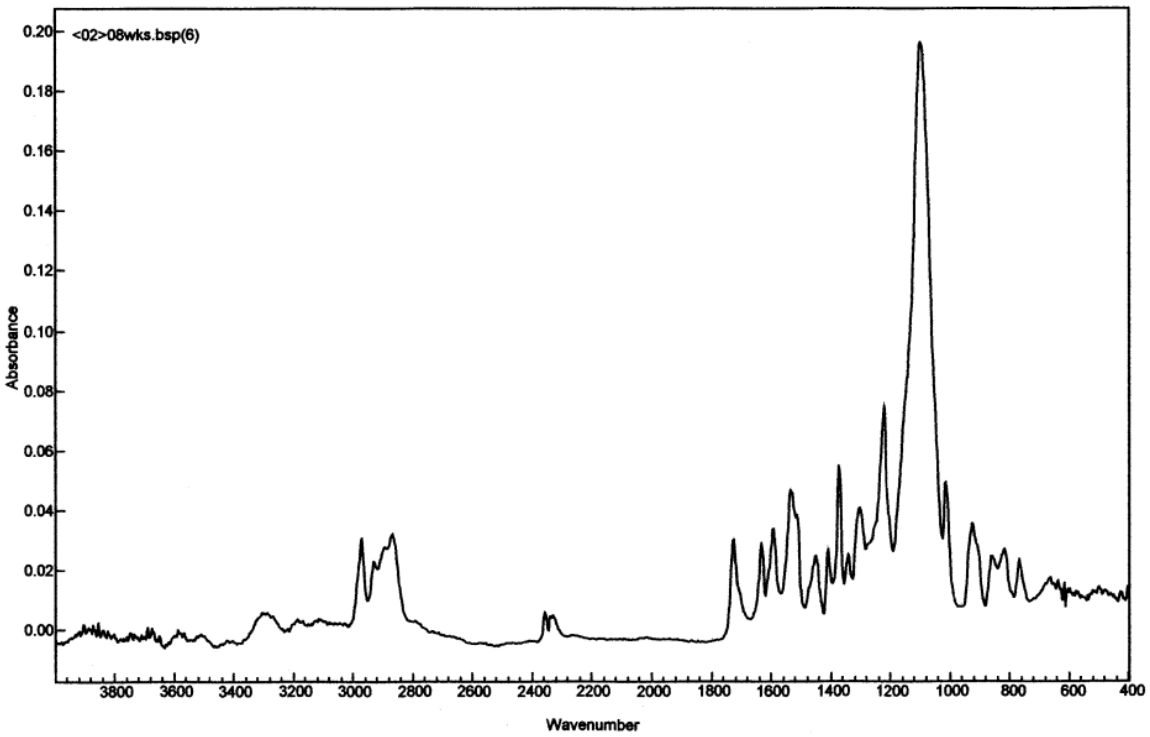

Figure B.30. PPG based polymer, 10% fluorinated, exposed for 08 weeks.

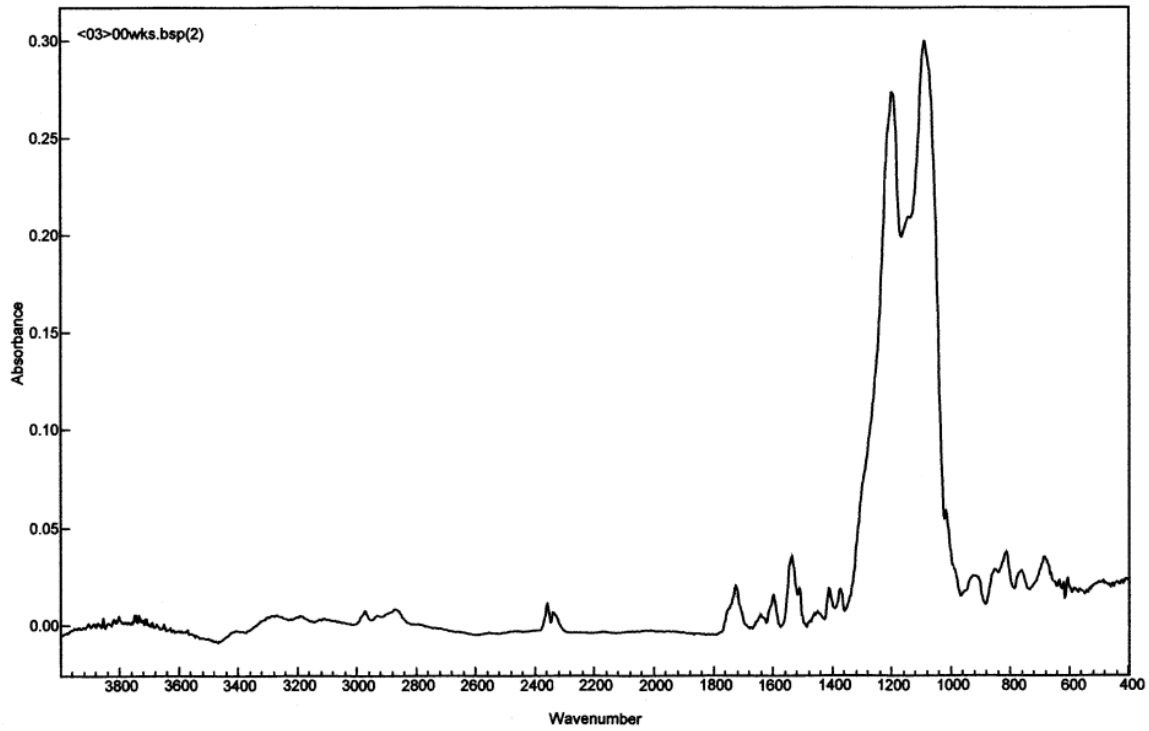

Figure B.31. PPG based polymer, 30% fluorinated, unexposed.

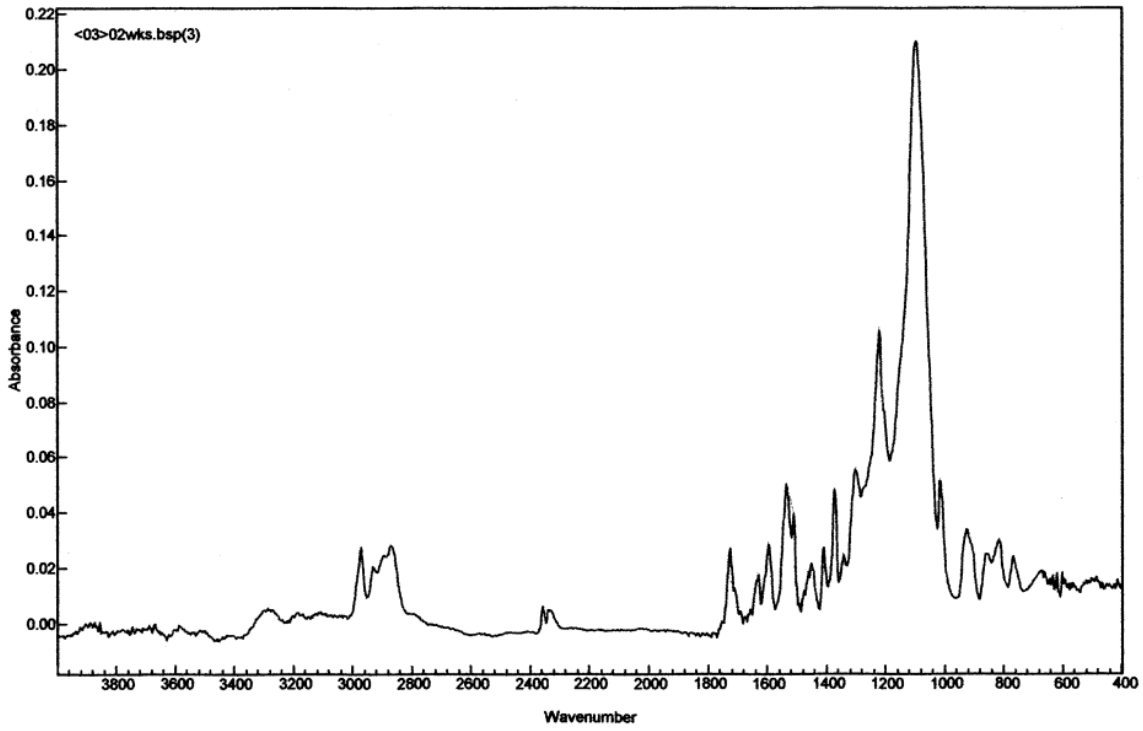

Figure B.32. PPG based polymer, 30% fluorinated, exposed for 02 weeks.

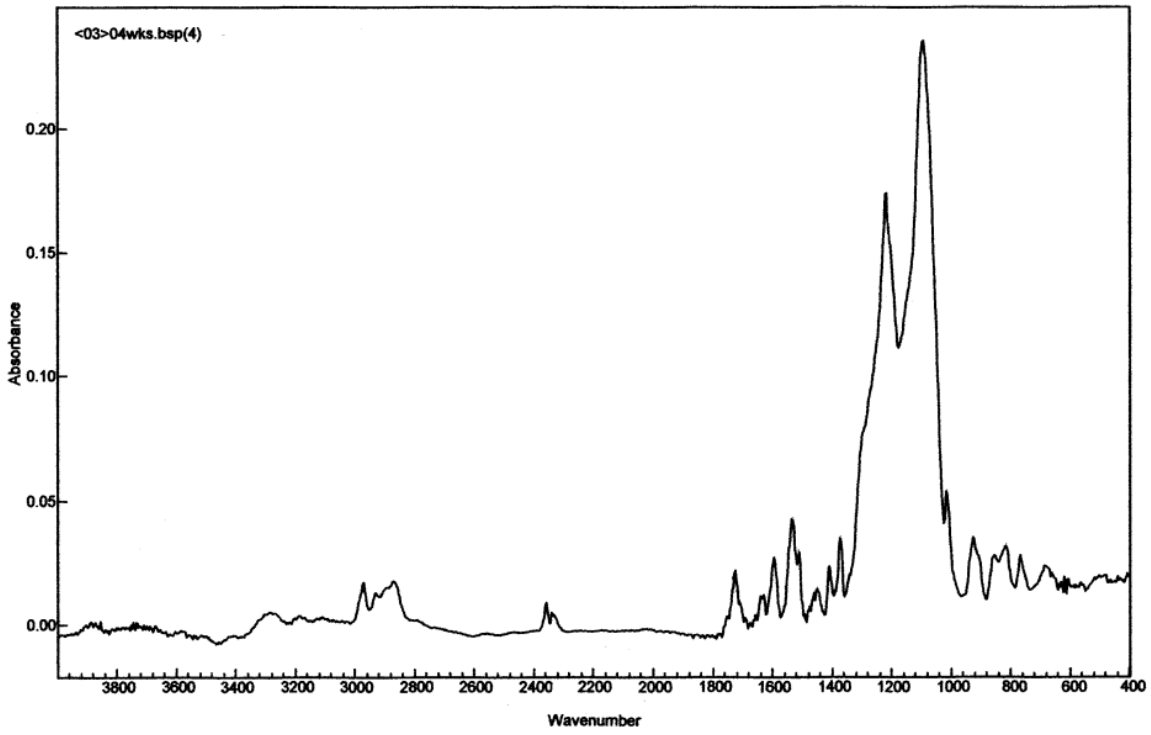

Figure B.33. PPG based polymer, 30% fluorinated, exposed for 04 weeks.

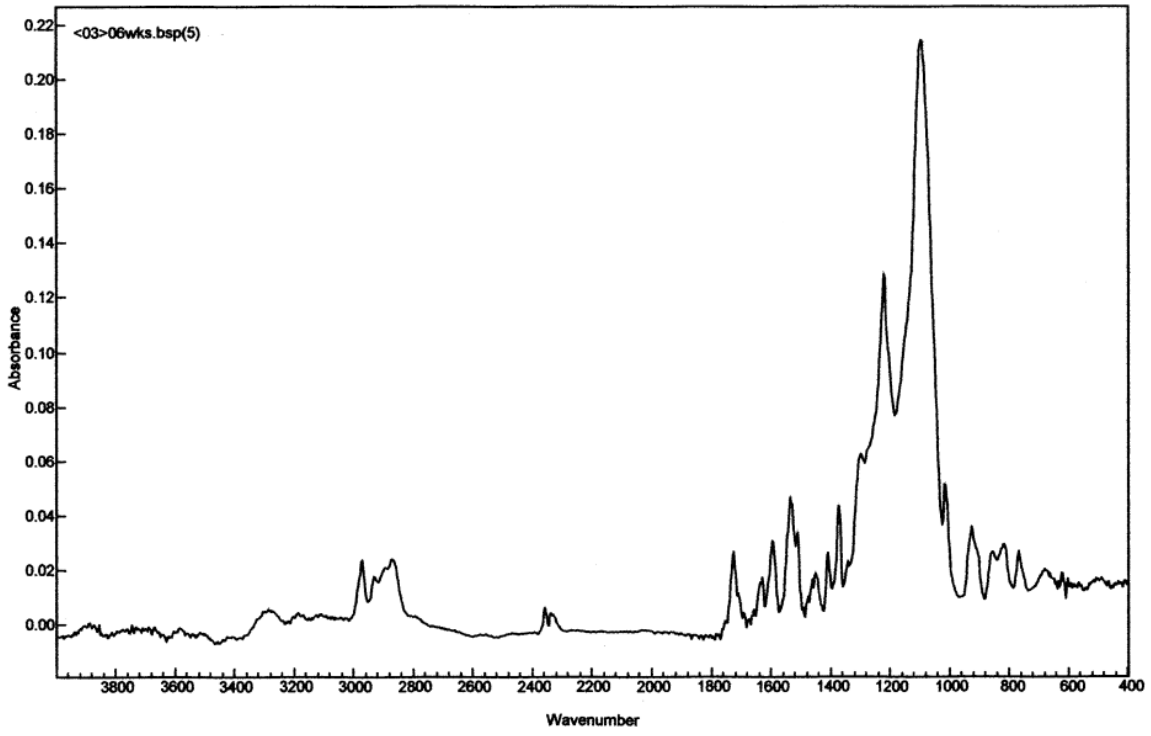

Figure B.34. PPG based polymer, 30% fluorinated, exposed for 06 weeks.

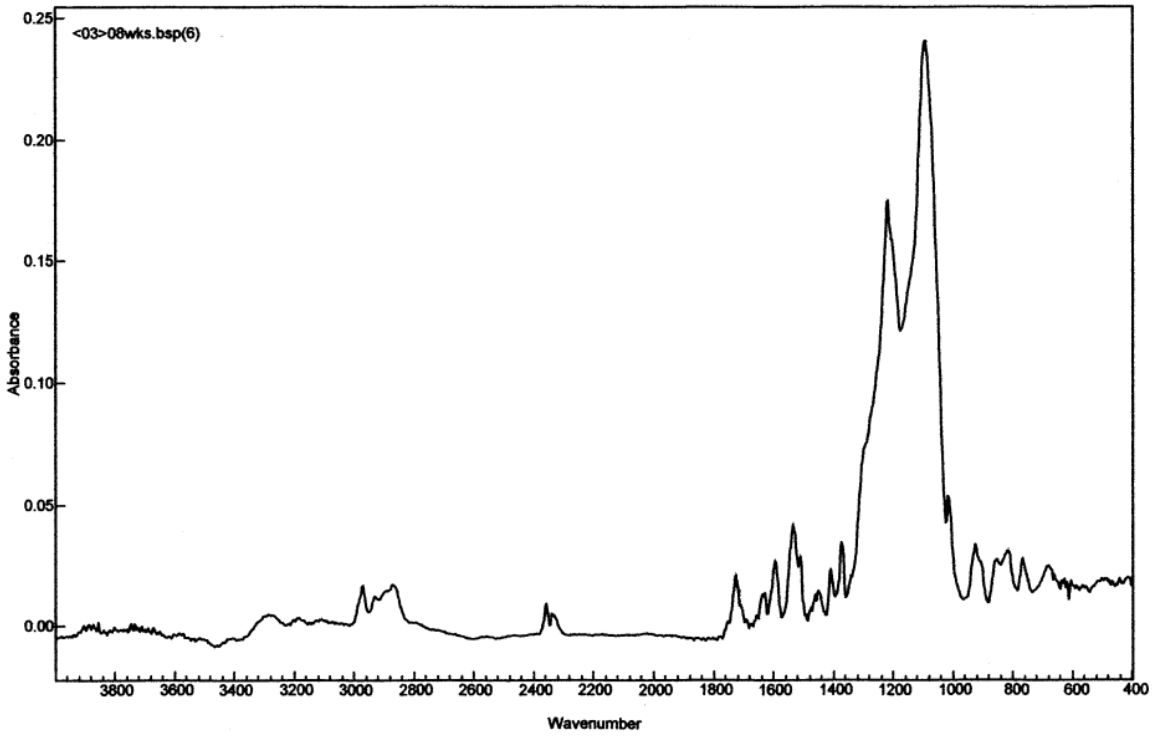

Figure B.35. PPG based polymer, 30% fluorinated, exposed for 08 weeks.

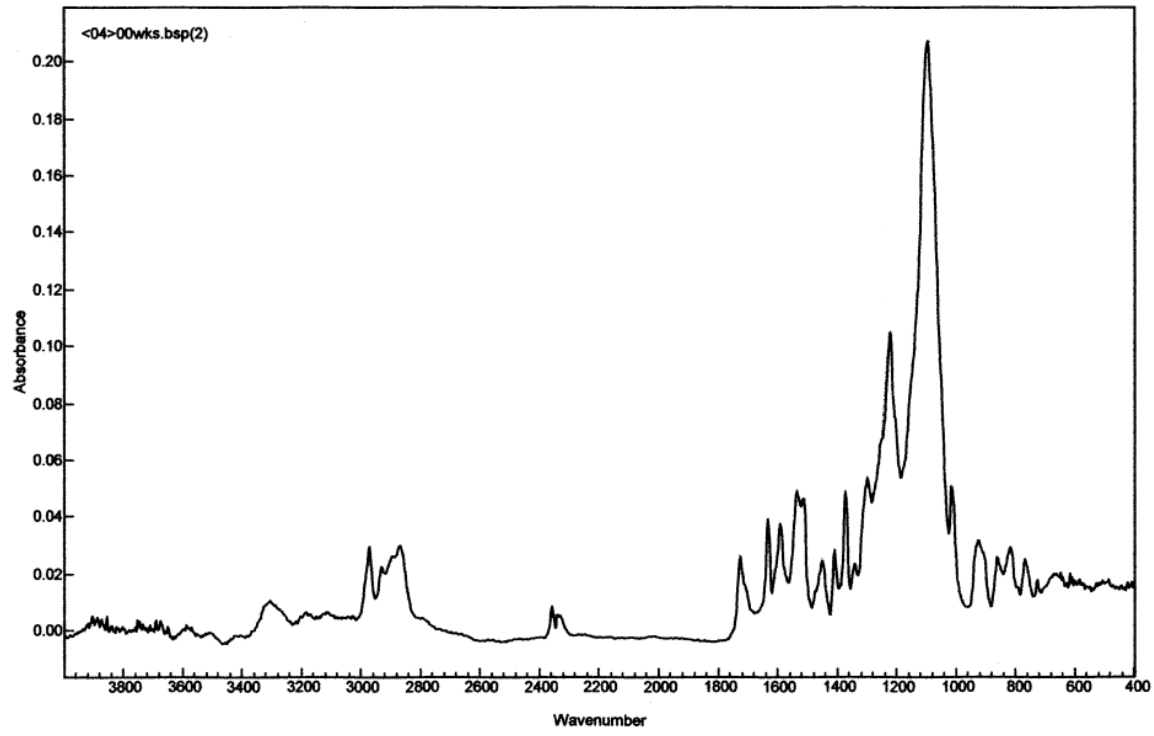

Figure B.36. PPG based polymer, 50% fluorinated, unexposed.

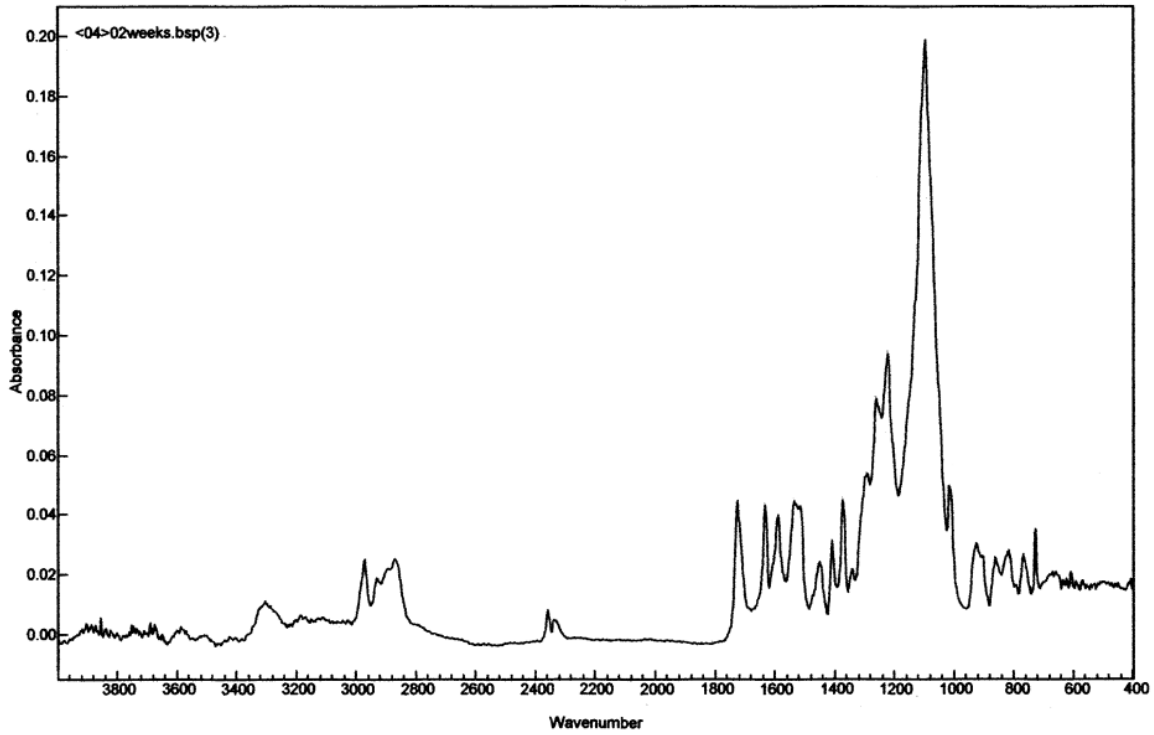

Figure B.37. PPG based polymer, 50% fluorinated, exposed for 02 weeks.

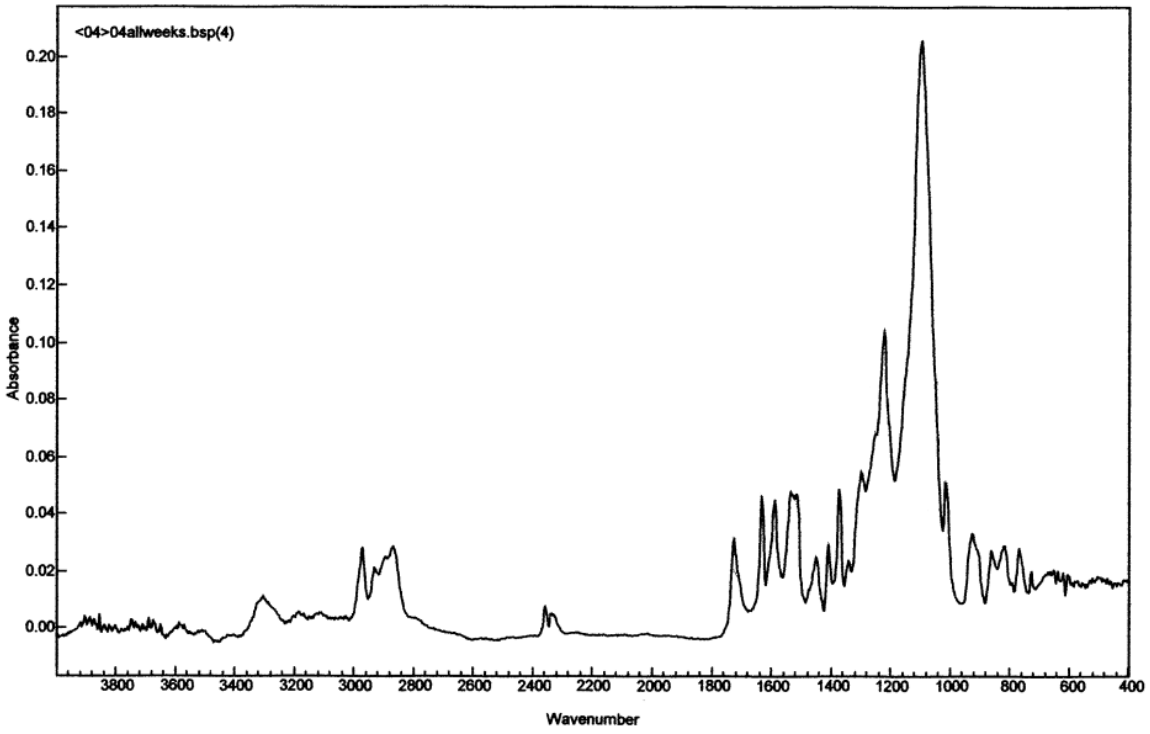

Figure B.38. PPG based polymer, 50% fluorinated, exposed for 04 weeks.

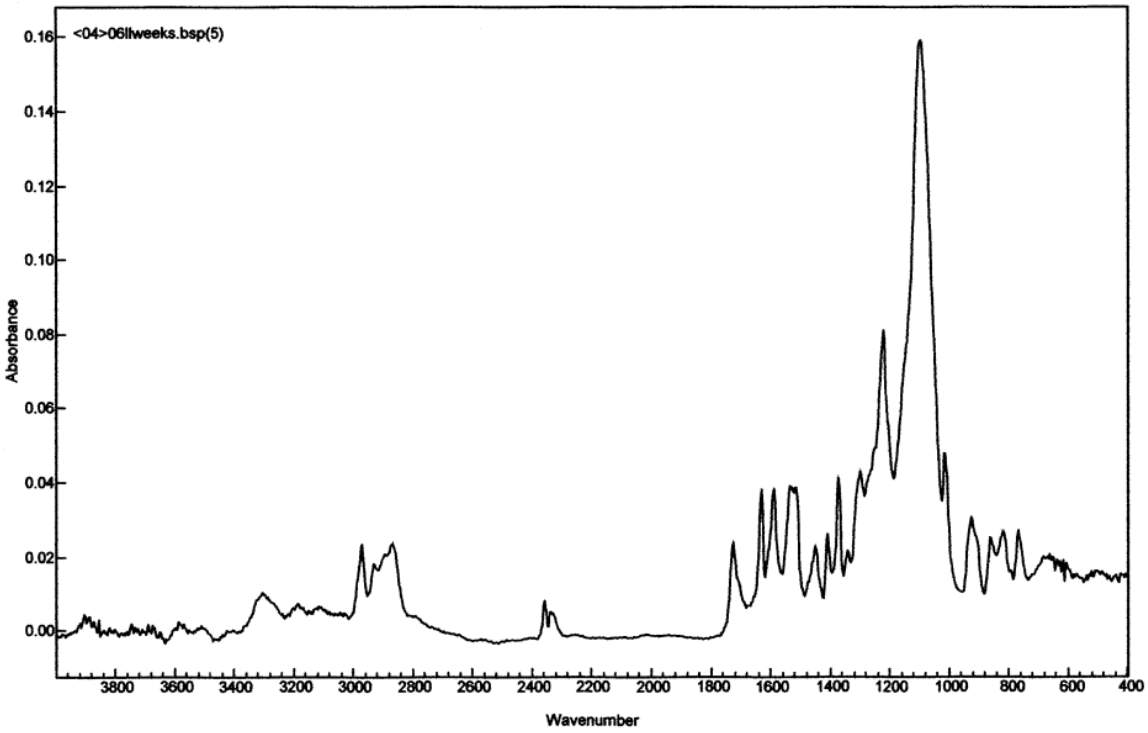

Figure B.39. PPG based polymer, 50% fluorinated, exposed for 06 weeks.

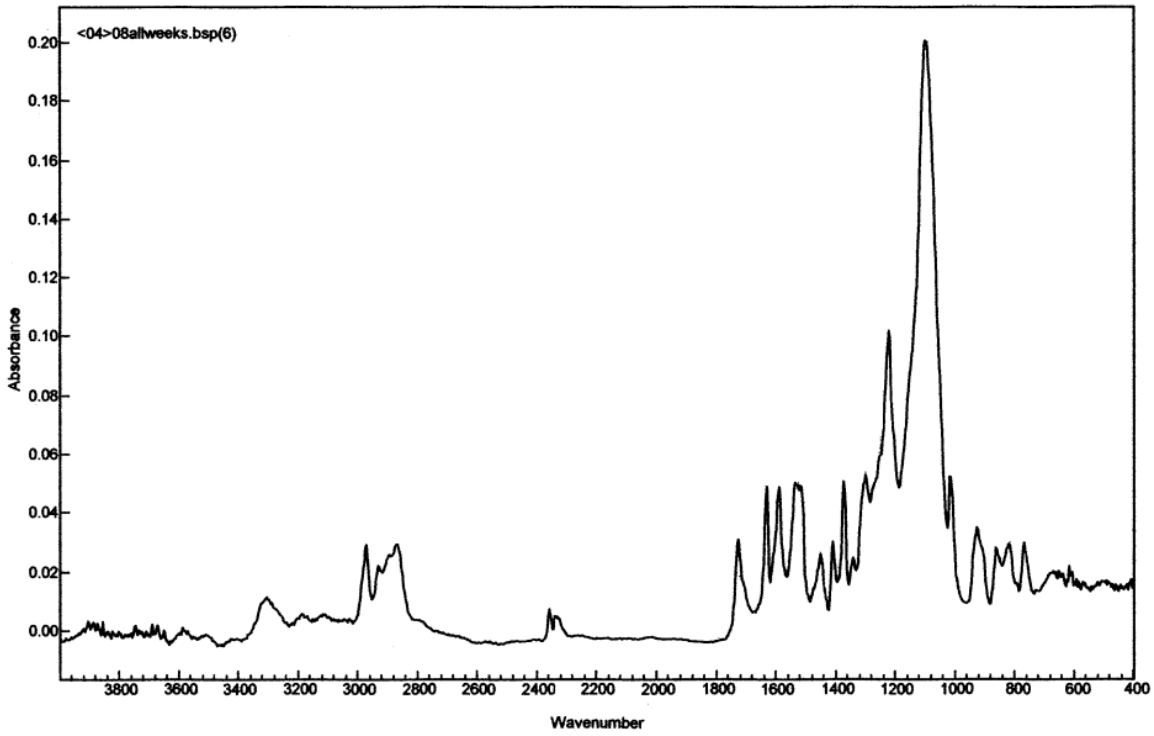

Figure B.40. PPG based polymer, 50% fluorinated, exposed for 08 weeks.

Appendix C: DMA code and results

Table C.1. Order of the figures on Appendix C.

	PTMG unexposed	PTMG 02 weeks	PTMG 08 weeks	PPG unexposed	PPG 02 weeks	PPG fin. week
E’	1 to 4	25 to 28	49 to 52	5 to 8	29 to 32	53 to 56
E”	9 to 12	33 to 36	57 to 60	13 to 16	37 to 40	61 to 64
Tan δ	17 to 20	41 to 44	65 to 68	21 to 24	45 to 48	69 to 72

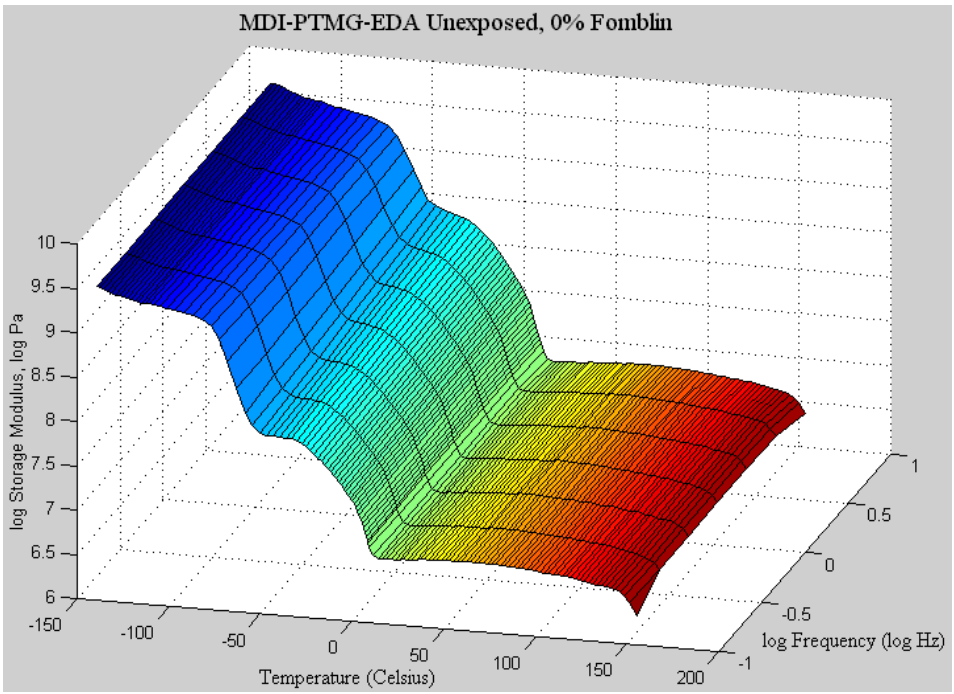

Figure C.1. PTMG based PU, non-fluorinated, unexposed, storage modulus versus temperature.

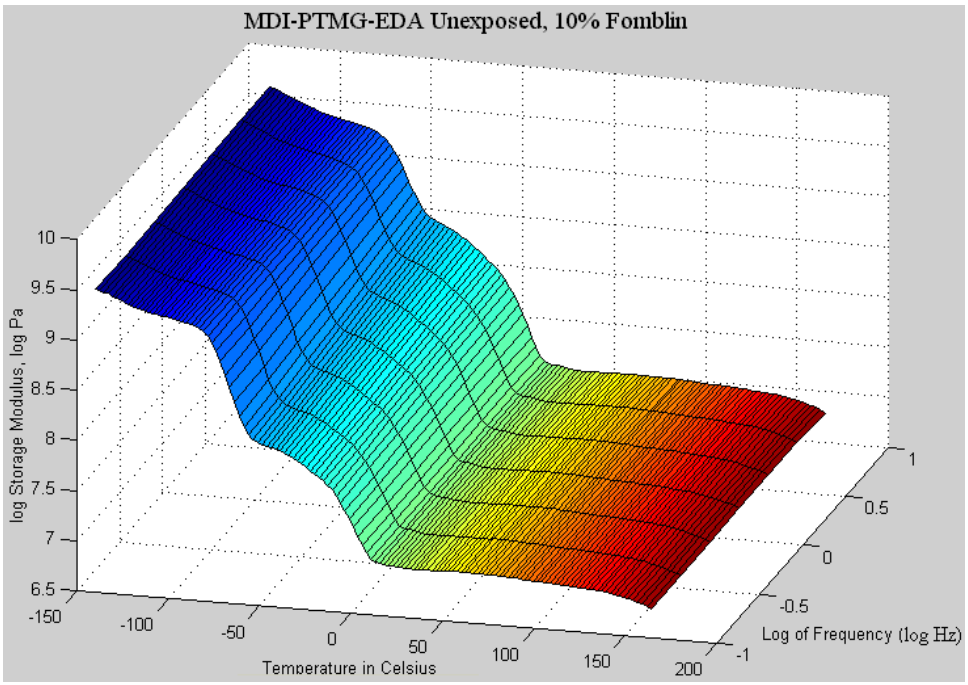

Figure C.2. PTMG based PU, 10% fluorinated, unexposed, storage modulus versus temperature.

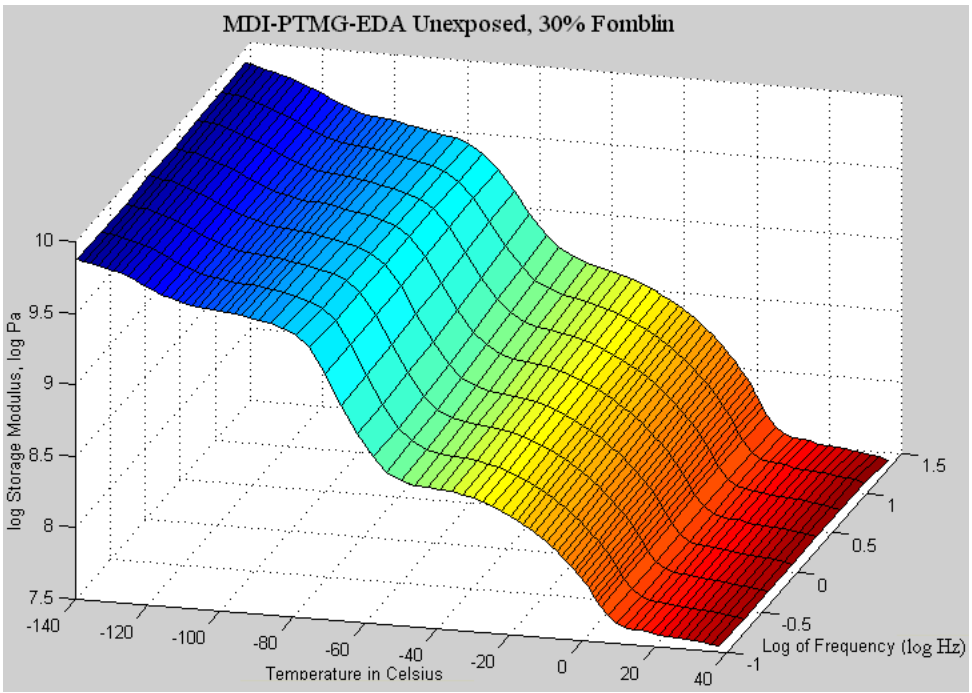

Figure C.3. PTMG based PU, 30% fluorinated, unexposed, storage modulus versus temperature.

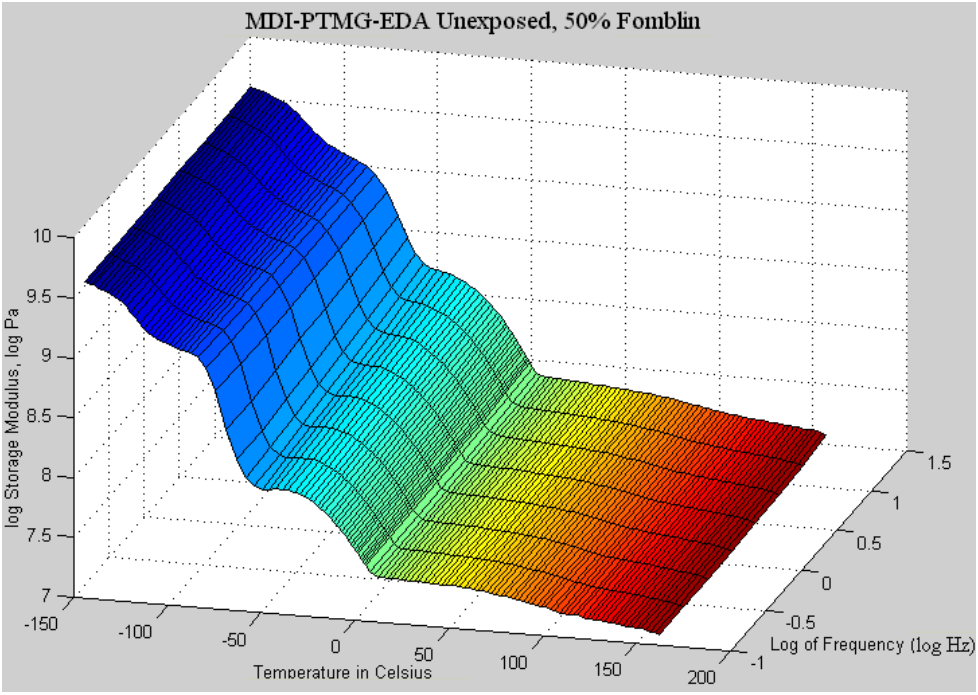

Figure C.4. PTMG based PU, 50% fluorinated, unexposed, storage modulus versus temperature.

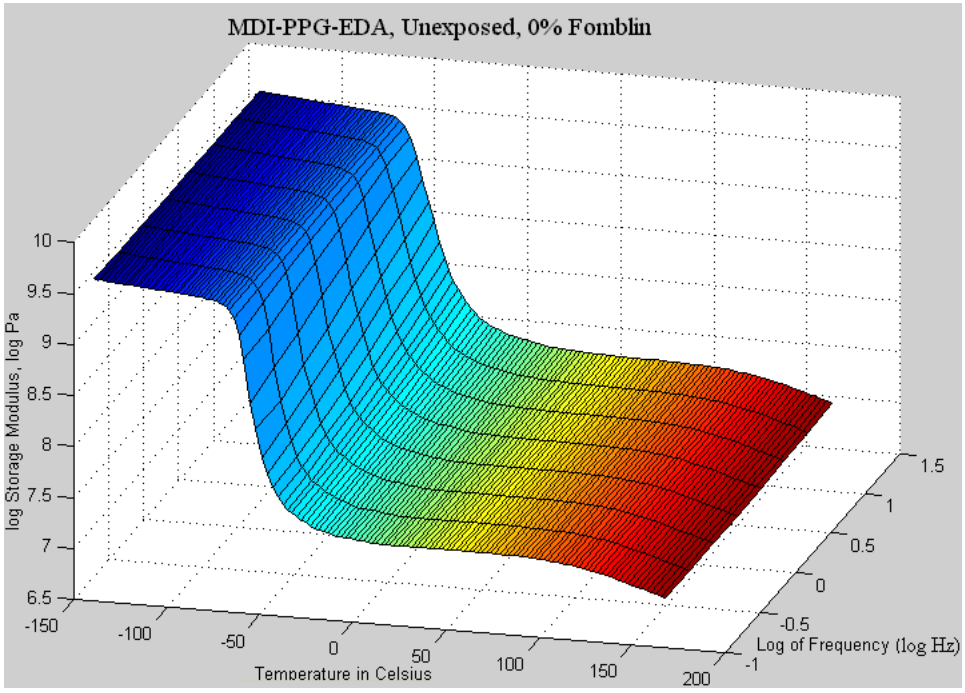

Figure C.5. PPG based PU, non-fluorinated, unexposed, storage modulus versus temperature.

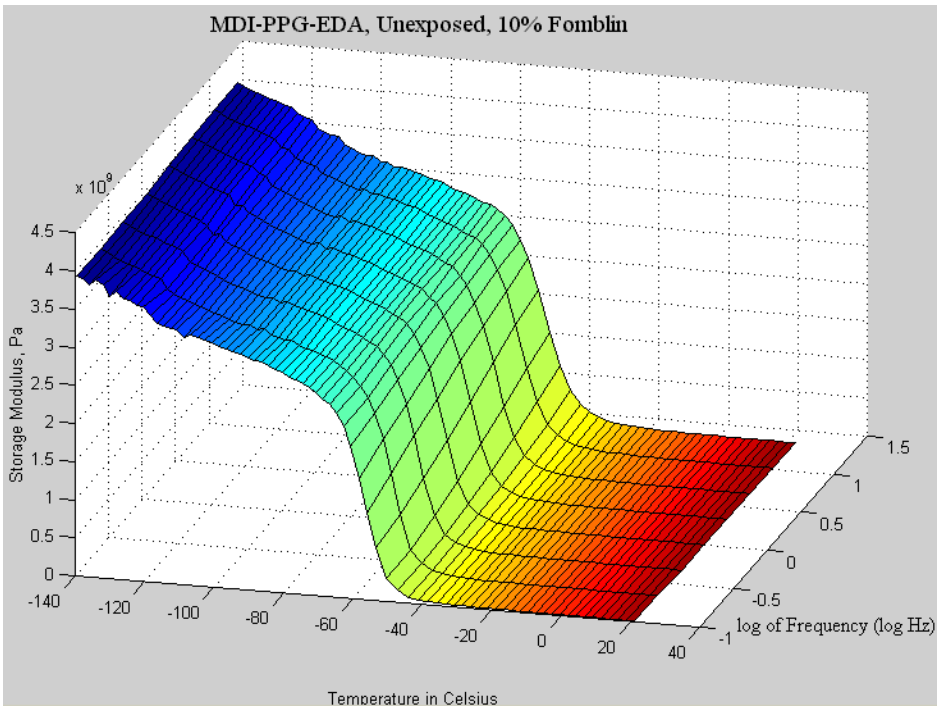

Figure C.6. PPG based PU, 10% fluorinated, unexposed, storage modulus versus temperature.

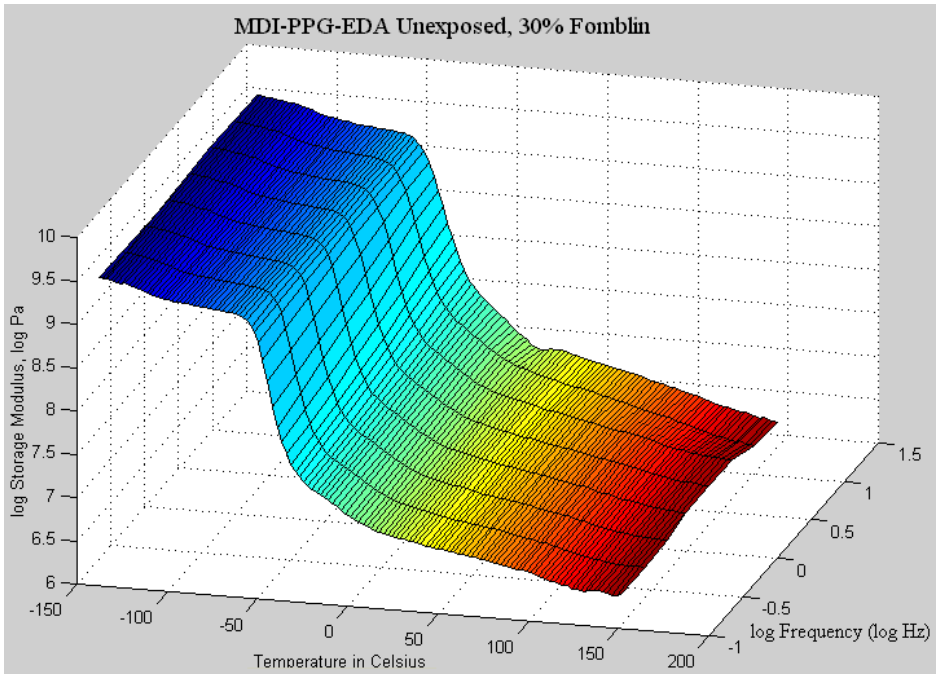

Figure C.7. PPG based PU, 30% fluorinated, unexposed, storage modulus versus temperature.

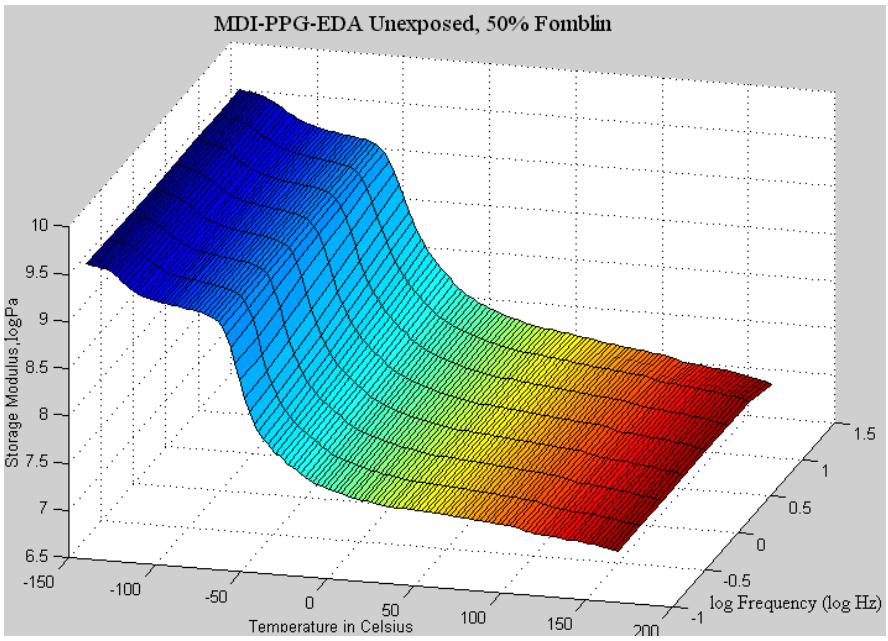

Figure C.8. PPG based PU, 50% fluorinated, unexposed, storage modulus versus temperature.

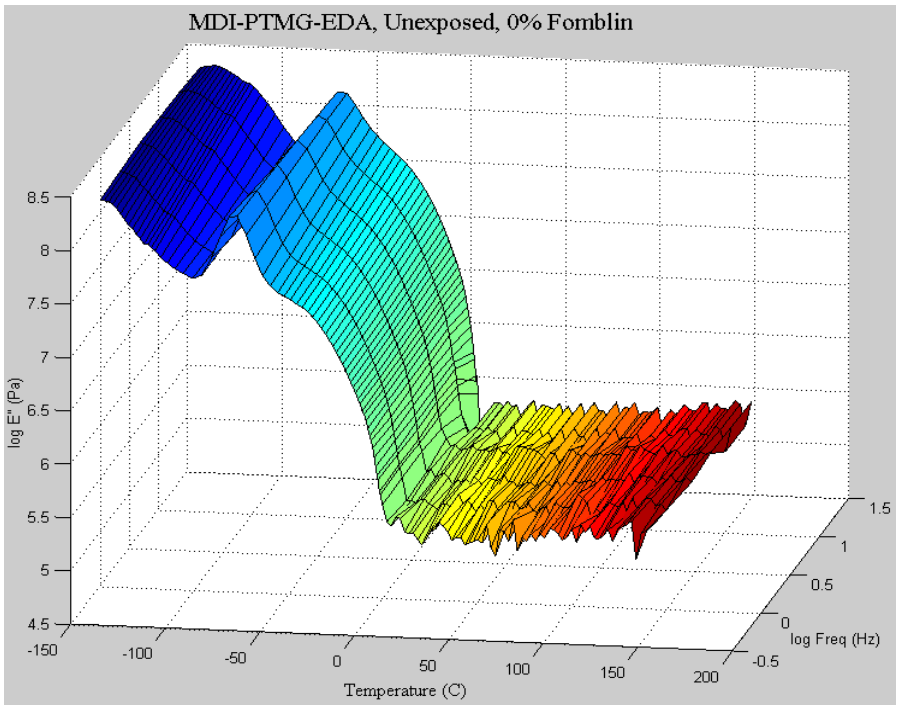

Figure C.9. PTMG based PU, non-fluorinated, unexposed, loss modulus versus temperature.

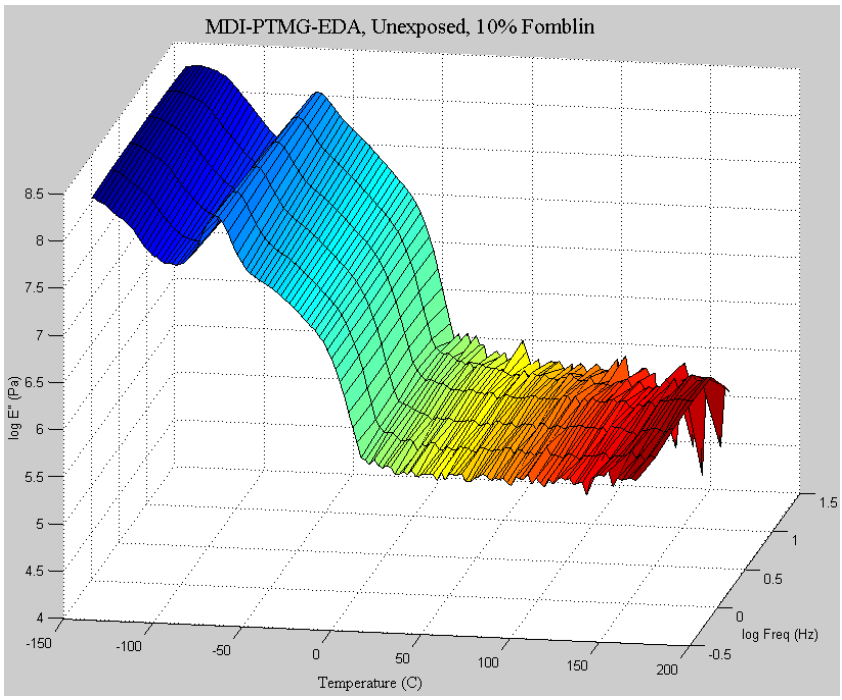

Figure C.10. PTMG based PU, 10% fluorinated, unexposed, loss modulus versus temperature.

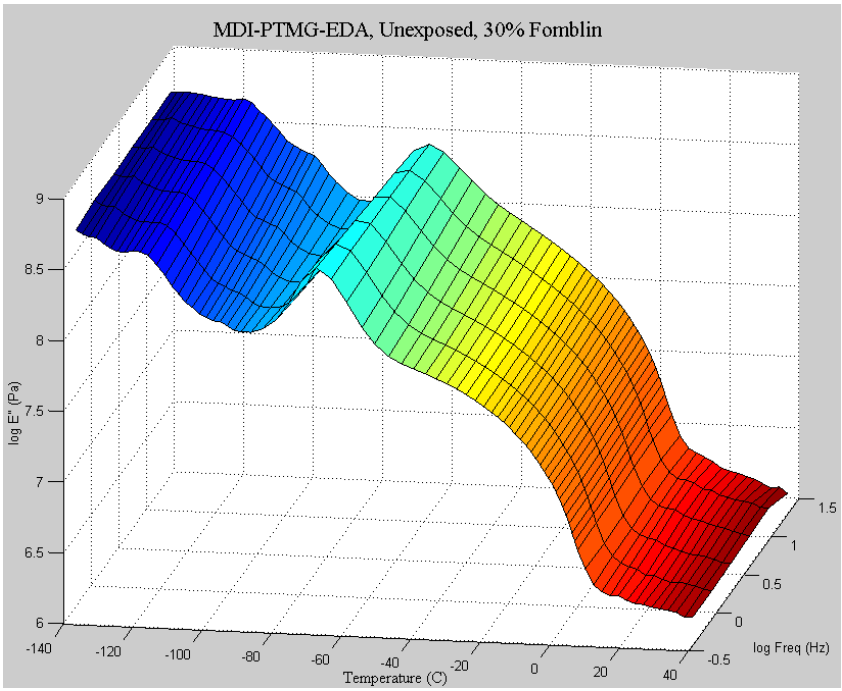

Figure C.11. PTMG based PU, 30% fluorinated, unexposed, loss modulus versus temperature.

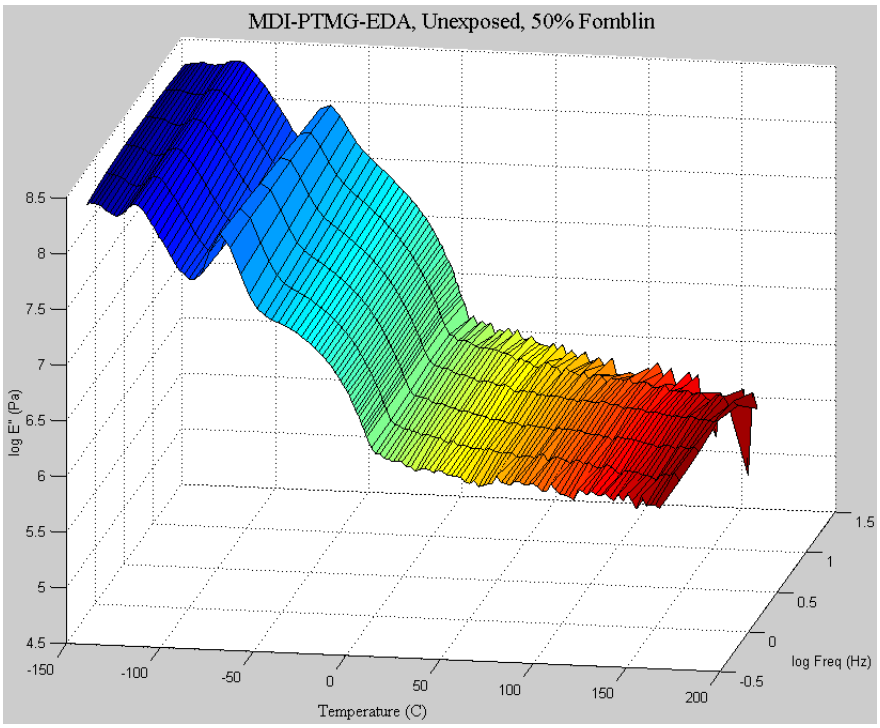

Figure C.12. PTMG based PU, 50% fluorinated, unexposed, loss modulus versus temperature.

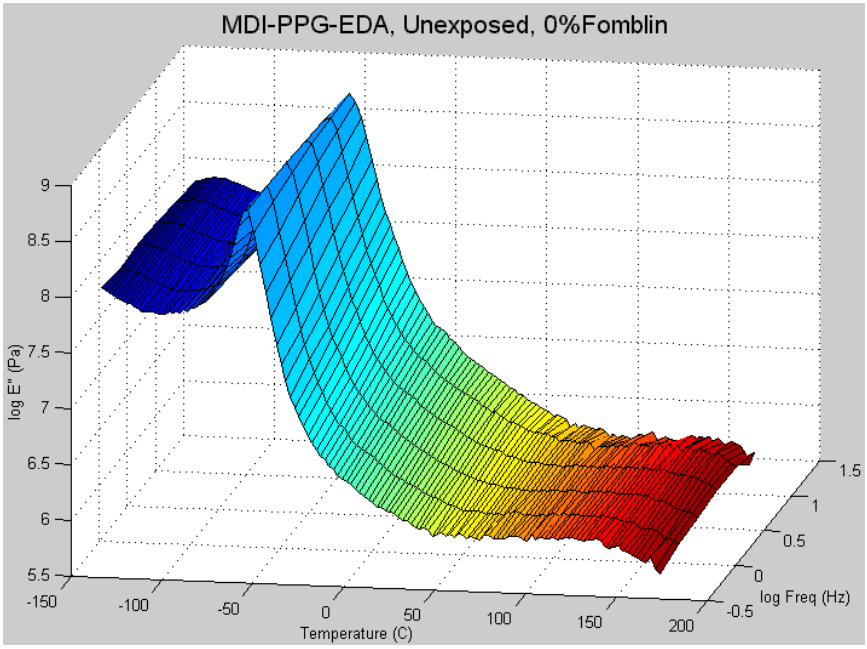

Figure C.13. PPG based PU, non-fluorinated, unexposed, loss modulus versus temperature.

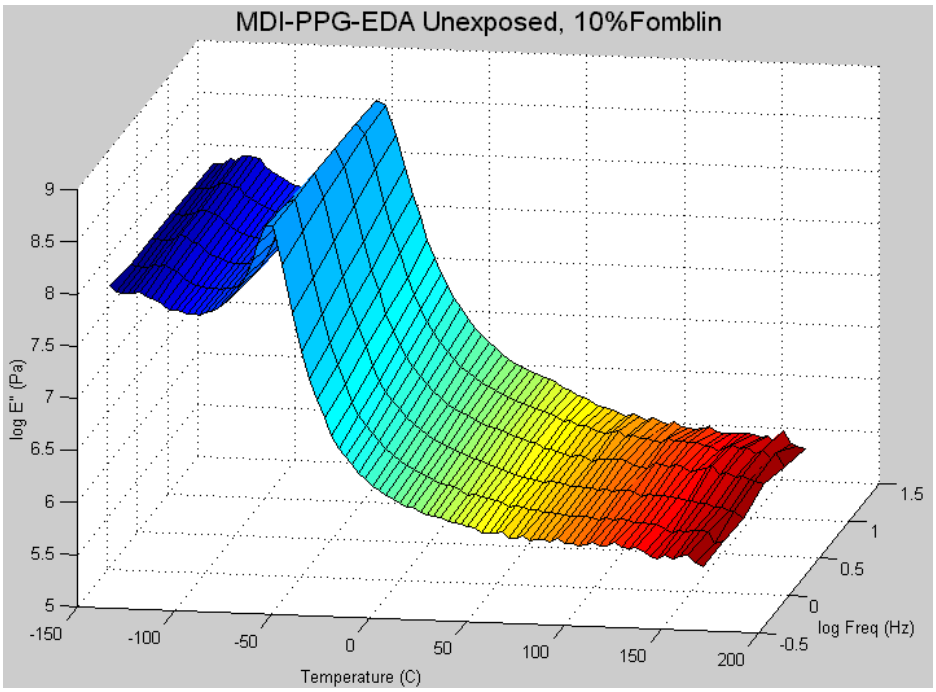

Figure C.14. PPG based PU, 10% fluorinated, unexposed, loss modulus versus temperature.

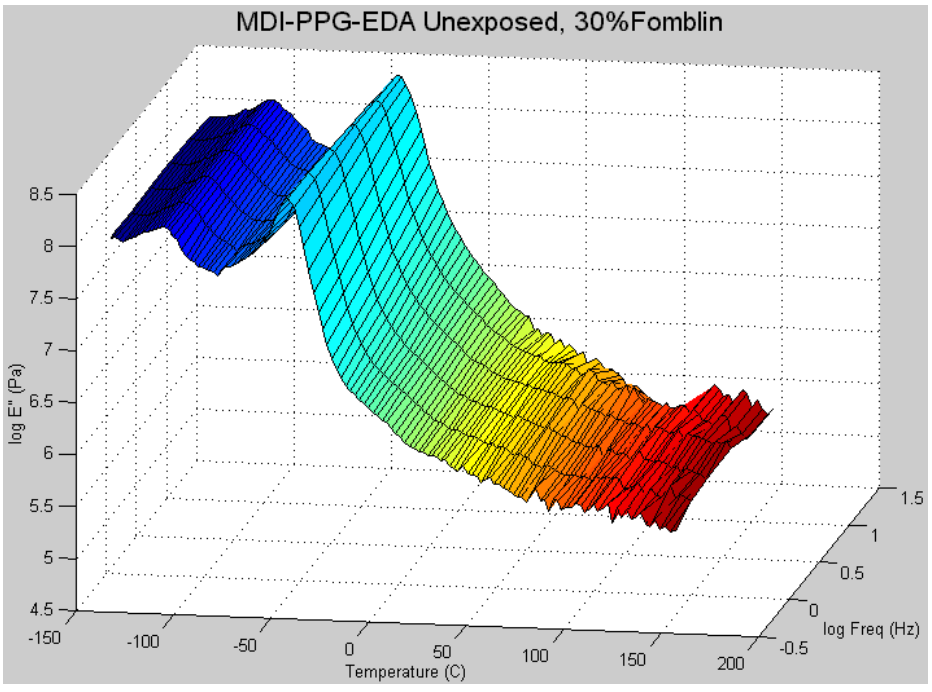

Figure C.15. PPG based PU, 30% fluorinated, unexposed, loss modulus versus temperature.

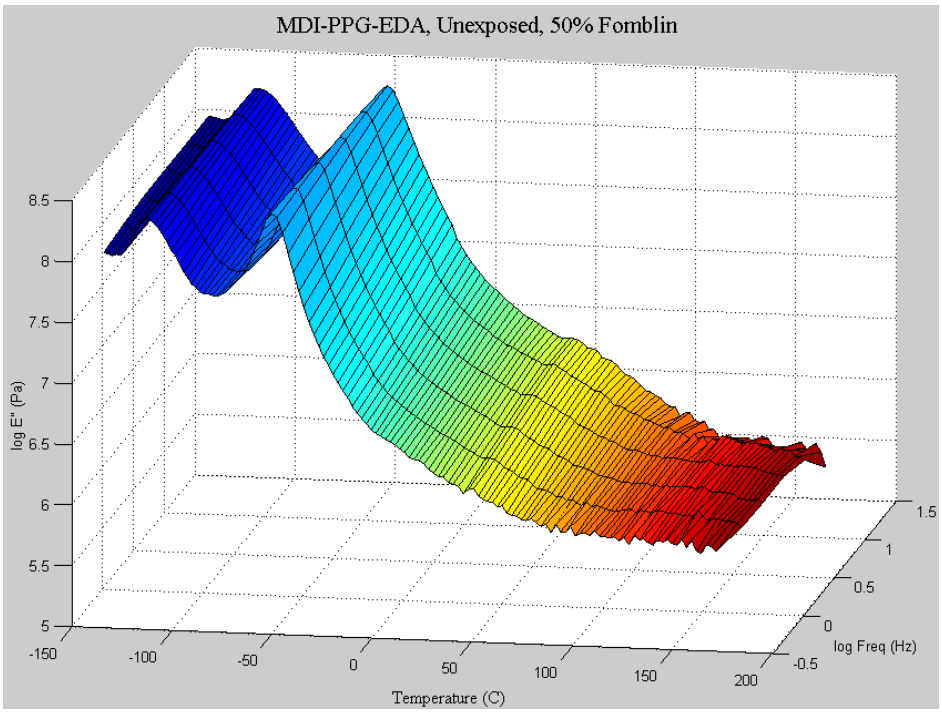

Figure C.16. PPG based PU, 50% fluorinated, unexposed, loss modulus versus temperature.

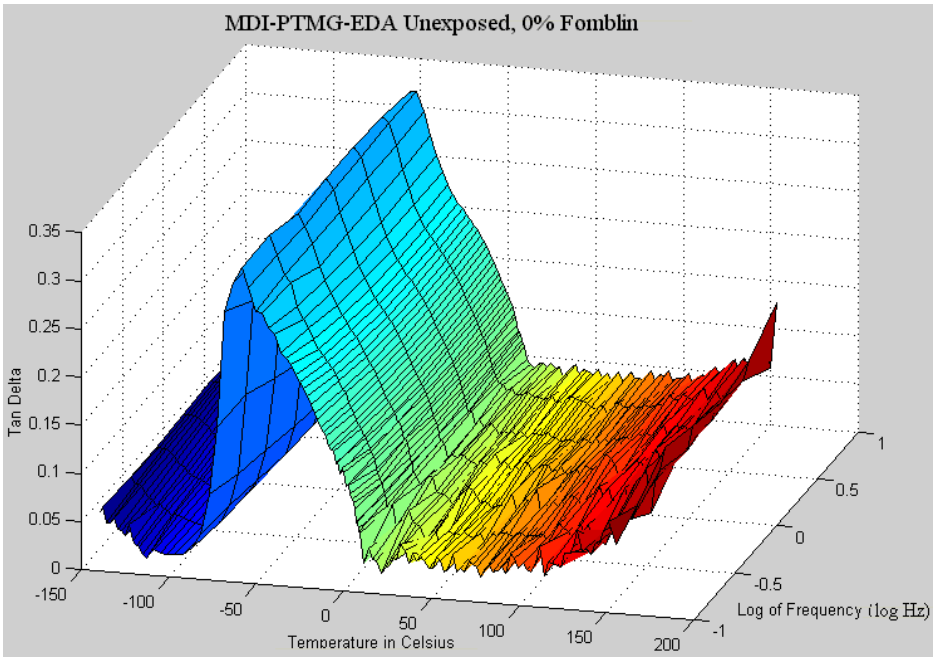

Figure C.17. PTMG based PU, non-fluorinated, unexposed, Tanδ versus temperature.

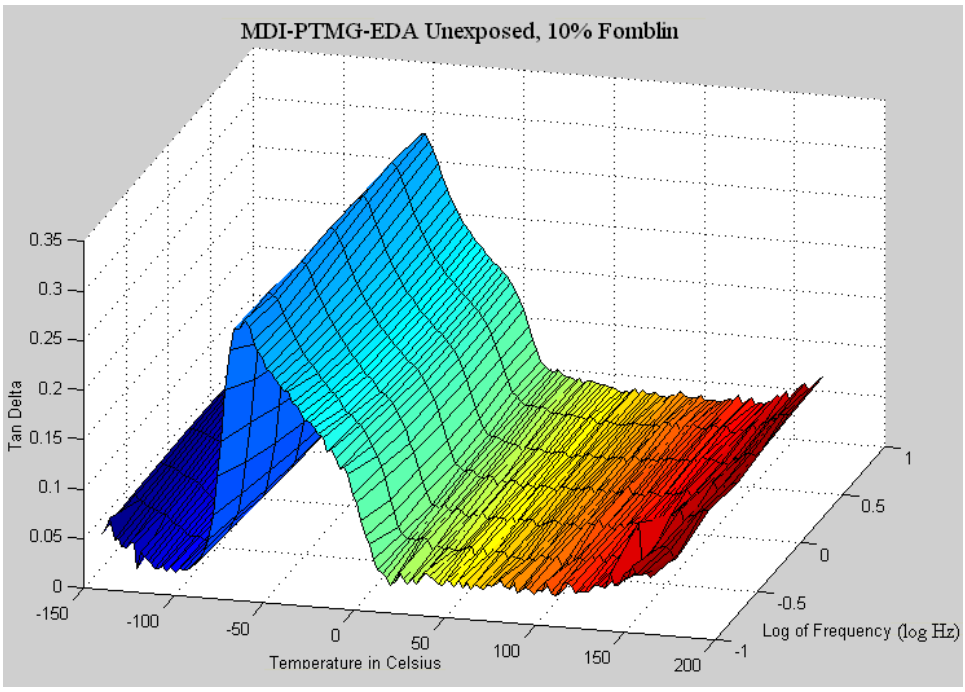

Figure C.18. PTMG based PU, 10% fluorinated, unexposed, Tanδ versus temperature.

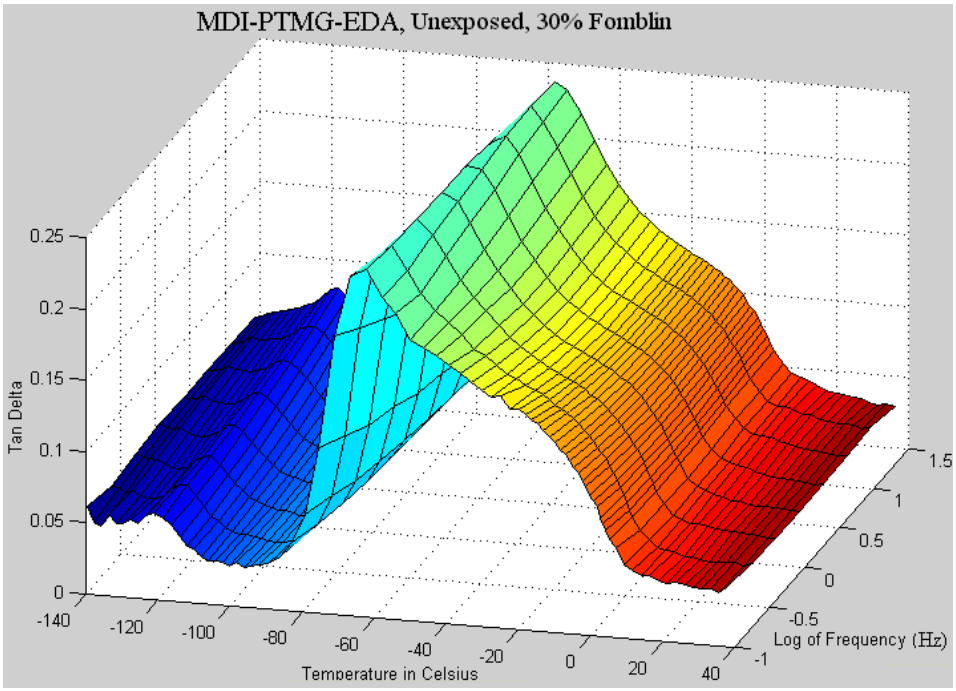

Figure C.19. PTMG based PU, 30% fluorinated, unexposed, Tanδ versus temperature.

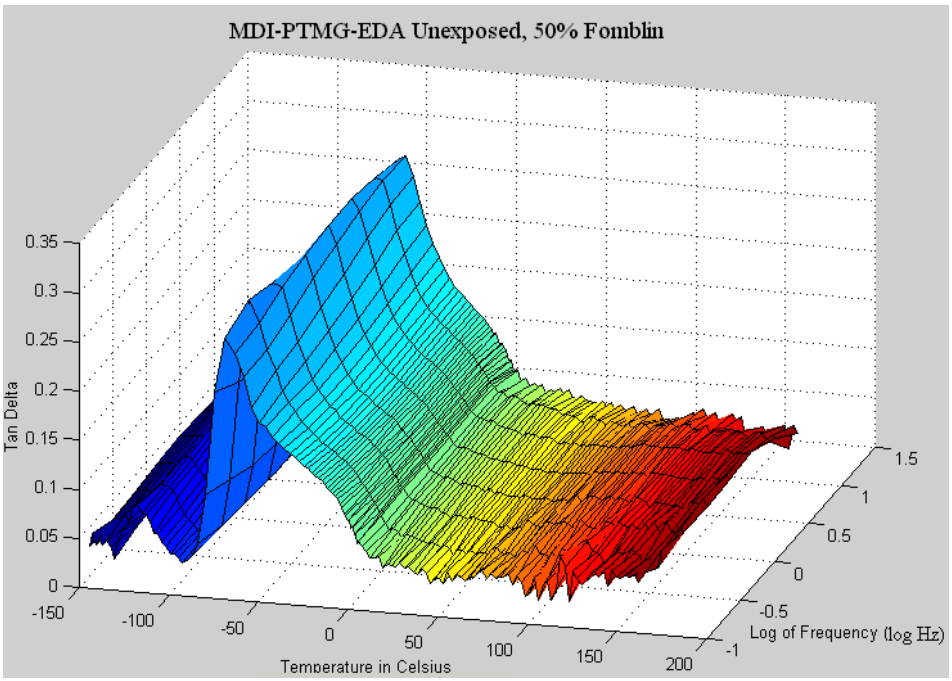

Figure C.20. PTMG based PU, 50% fluorinated, unexposed, Tanδ versus temperature.

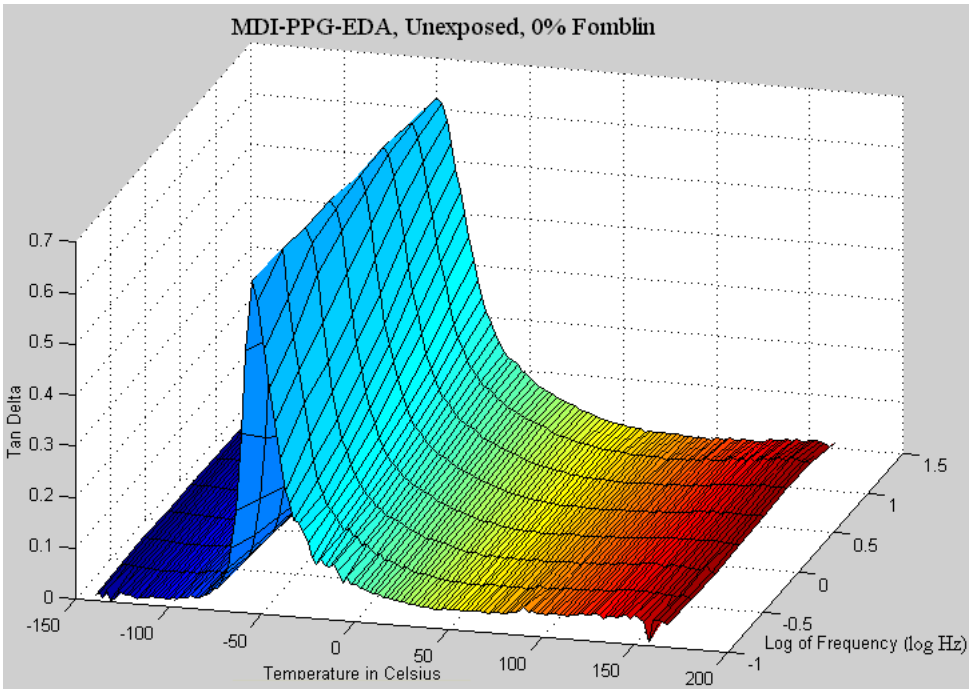

Figure C.21. PPG based PU, non-fluorinated, unexposed, Tanδ versus temperature.

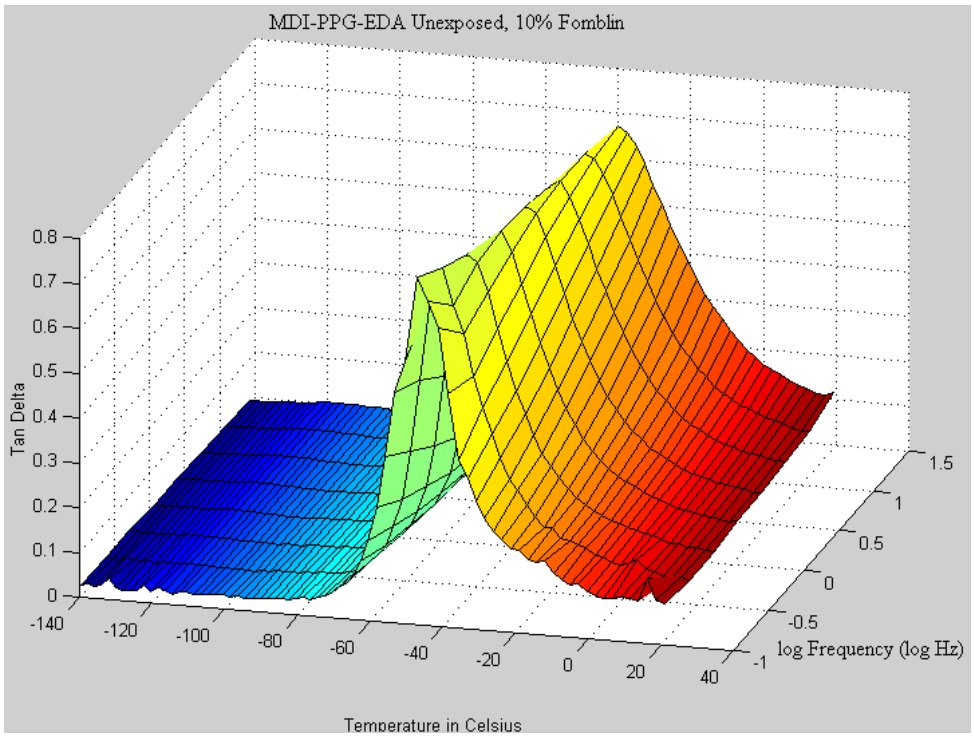

Figure C.22. PPG based PU, 10% fluorinated, unexposed, Tanδ versus temperature.

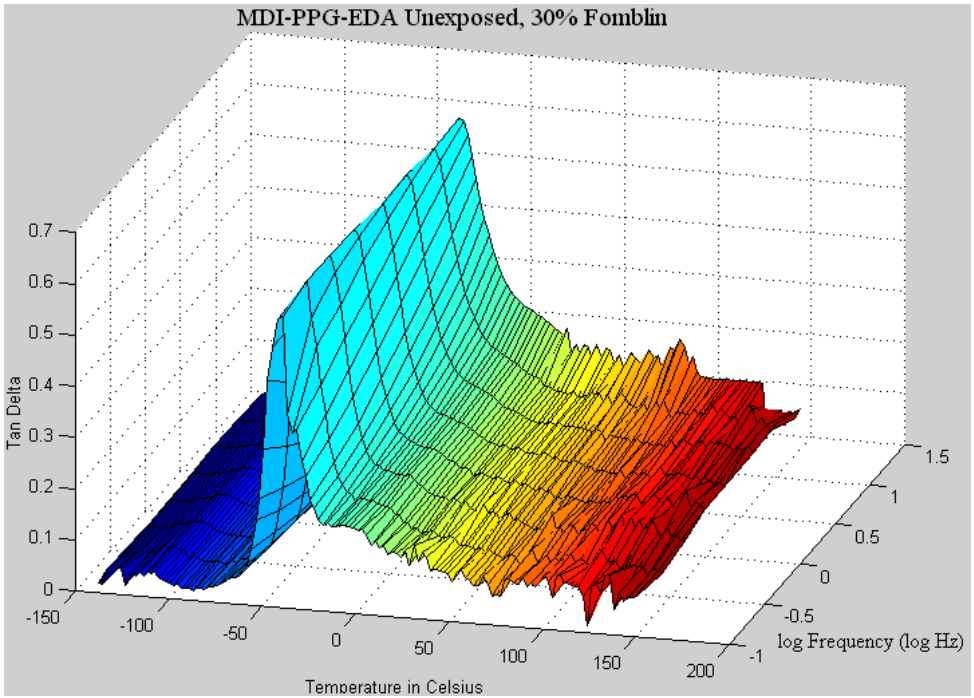

Figure C.23. PPG based PU, 30% fluorinated, unexposed, Tanδ versus temperature.

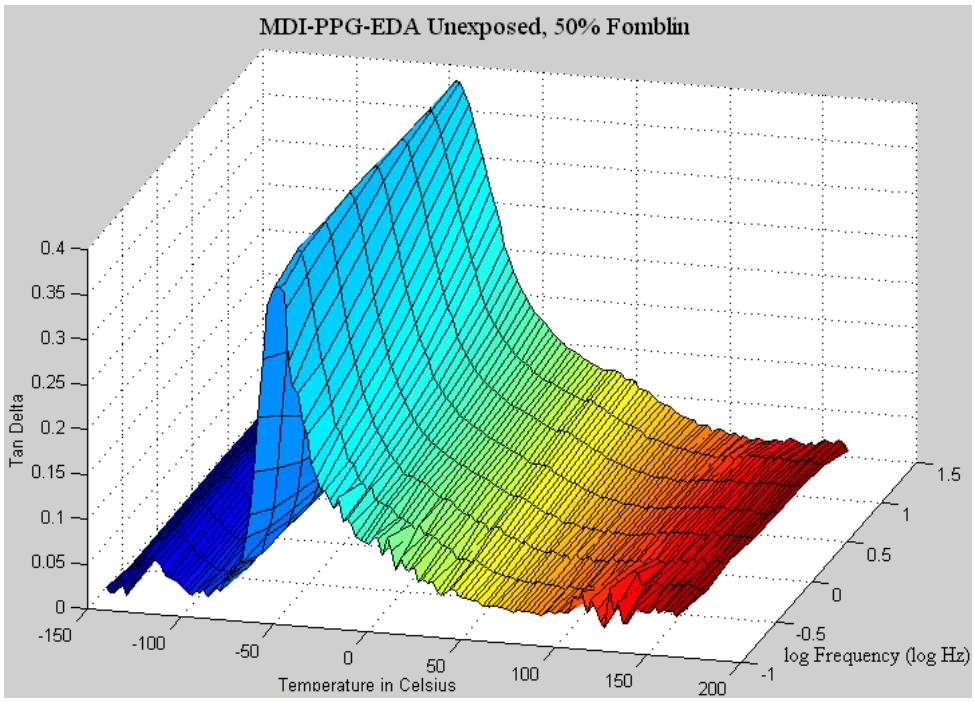

Figure C.24. PPG based PU, 50% fluorinated, unexposed, Tanδ versus temperature.

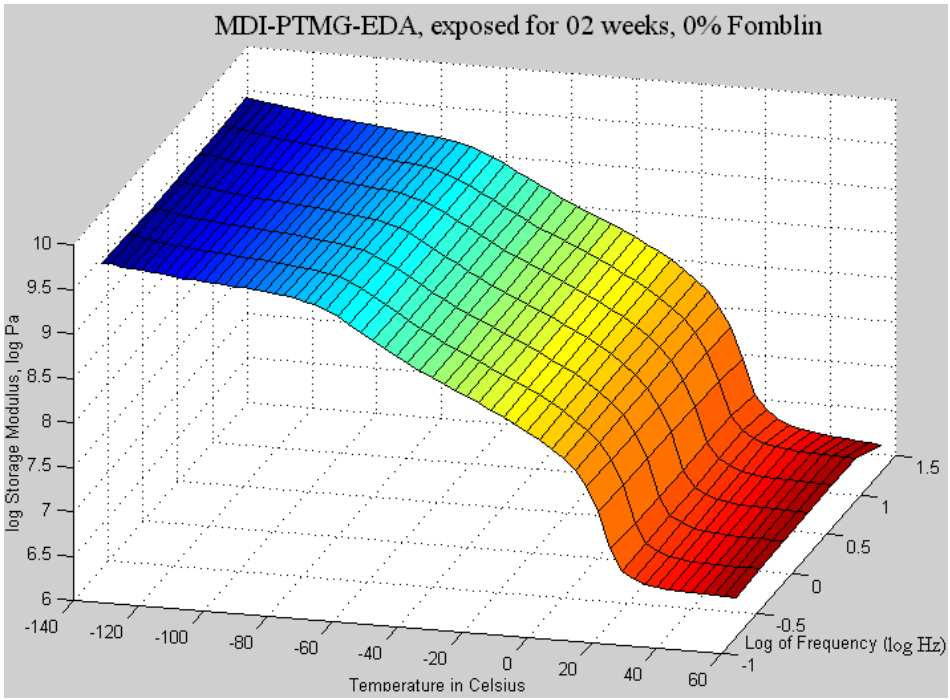

Figure C.25. PTMG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

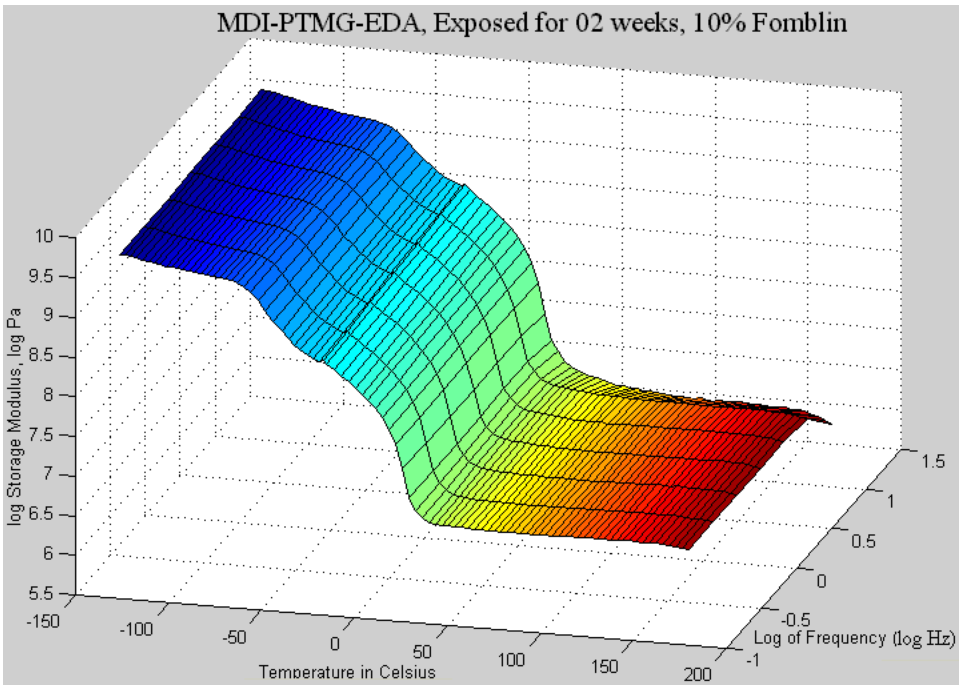

Figure C.26. PTMG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

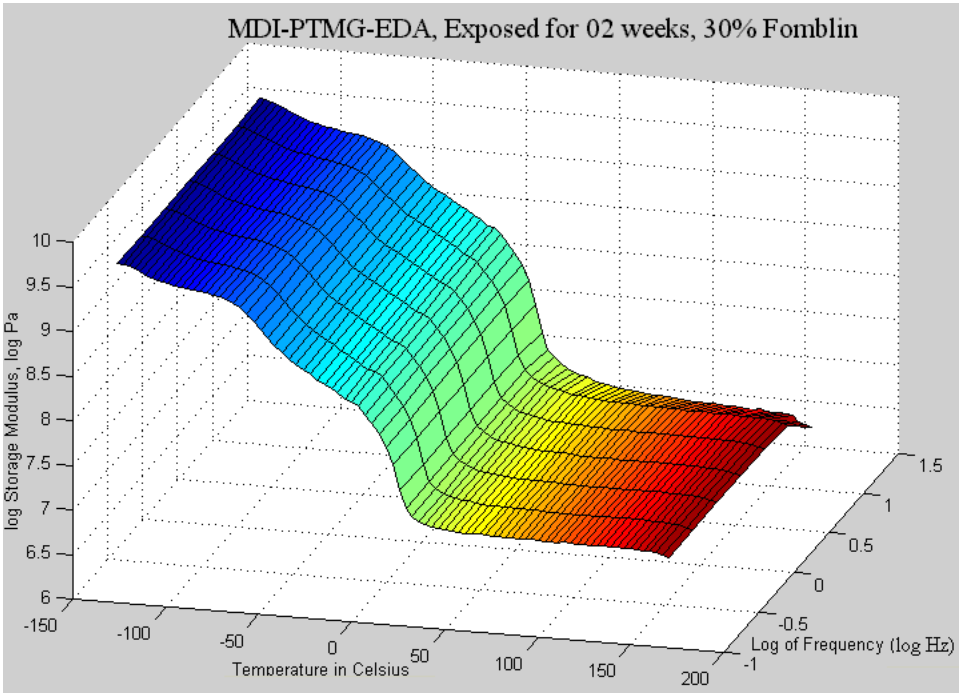

Figure C.27. PTMG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

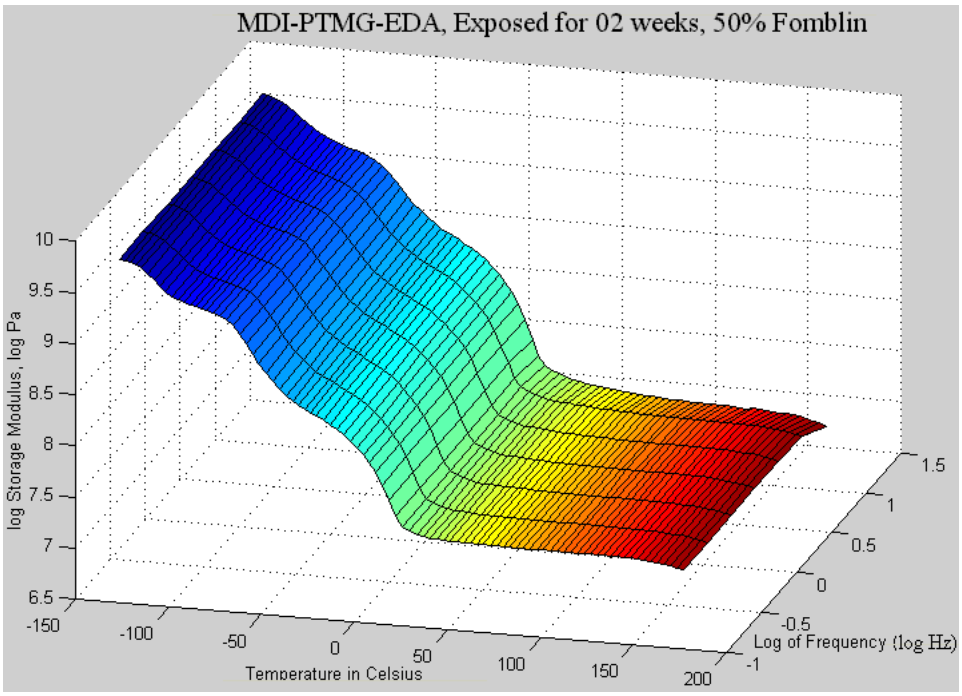

Figure C.28. PTMG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

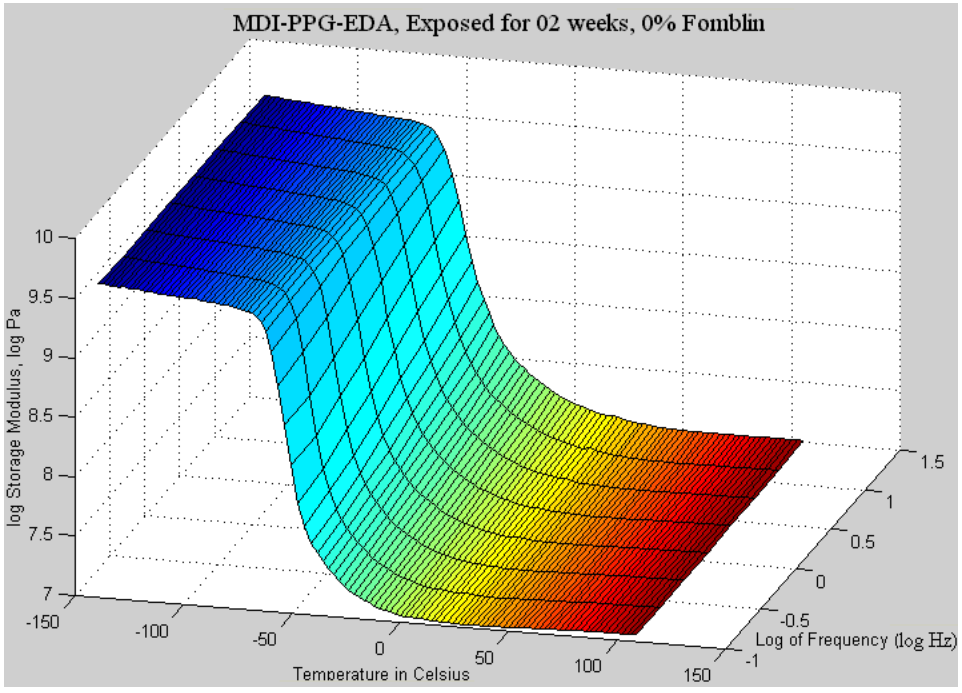

Figure C.29. PPG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

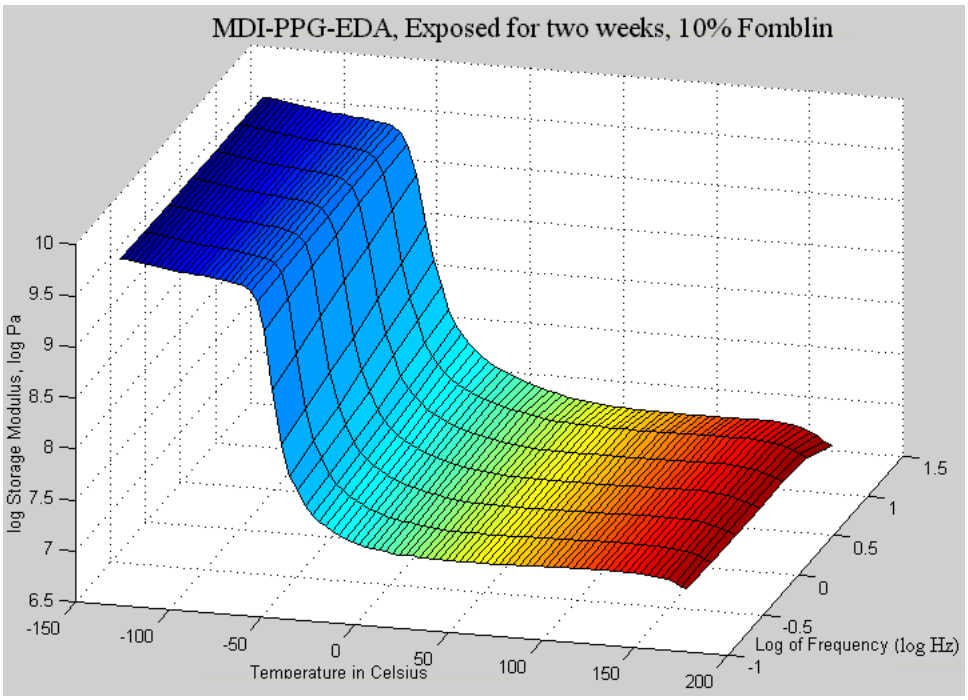

Figure C.30. PPG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

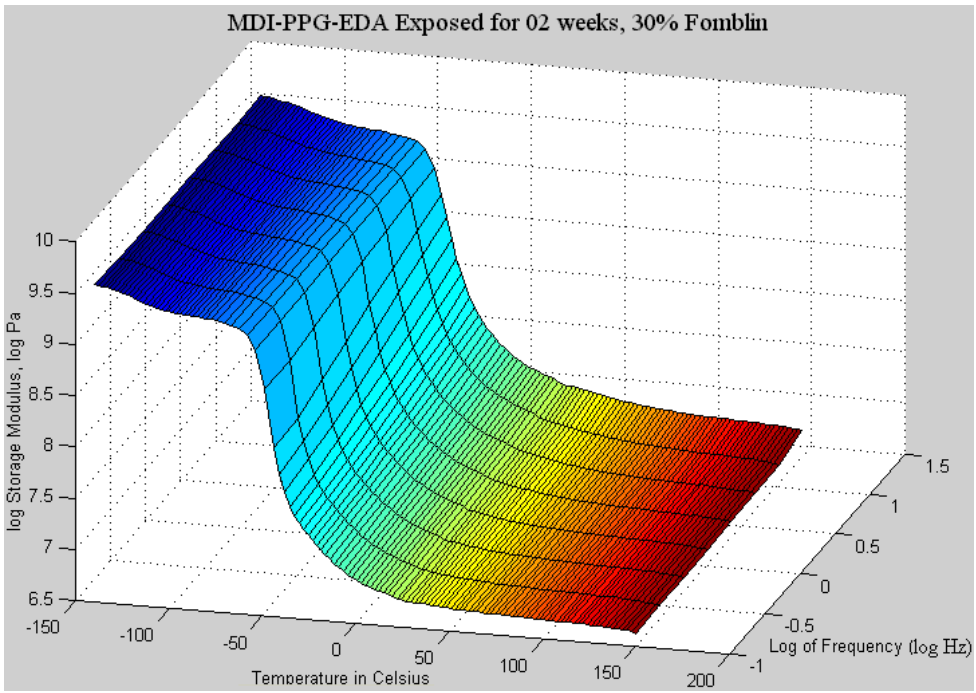

Figure C.31. PPG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

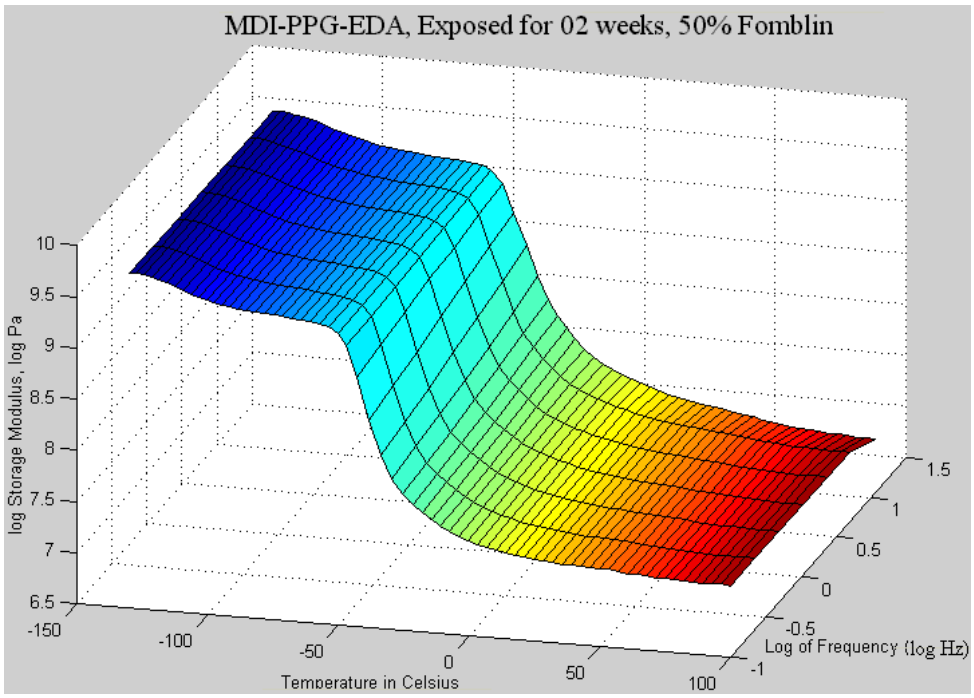

Figure C.32. PPG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, storage modulus versus temperature.

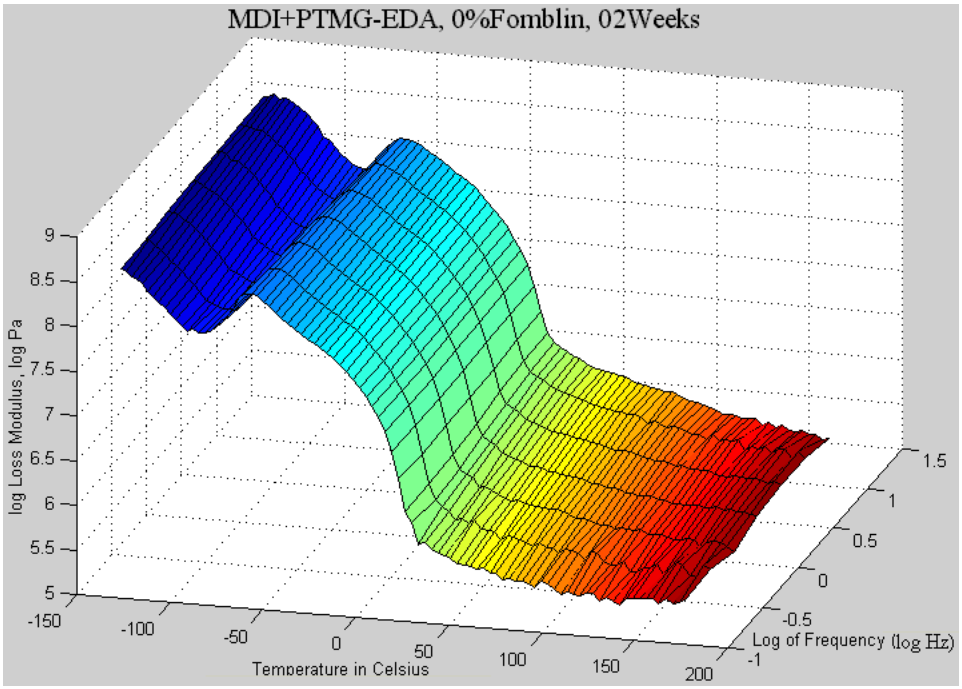

Figure C.33. PTMG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

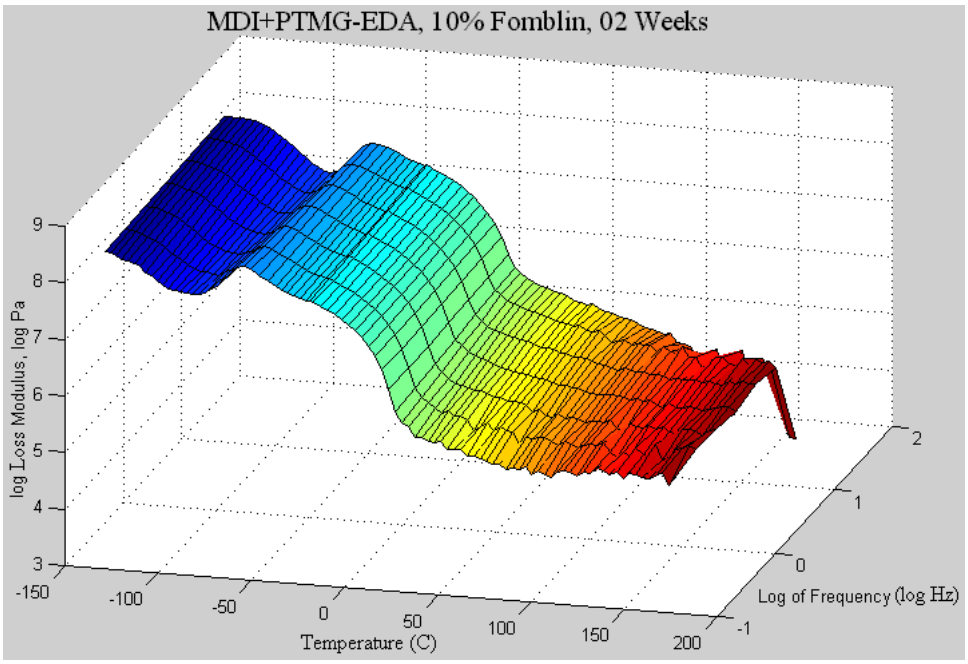

Figure C.34. PTMG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

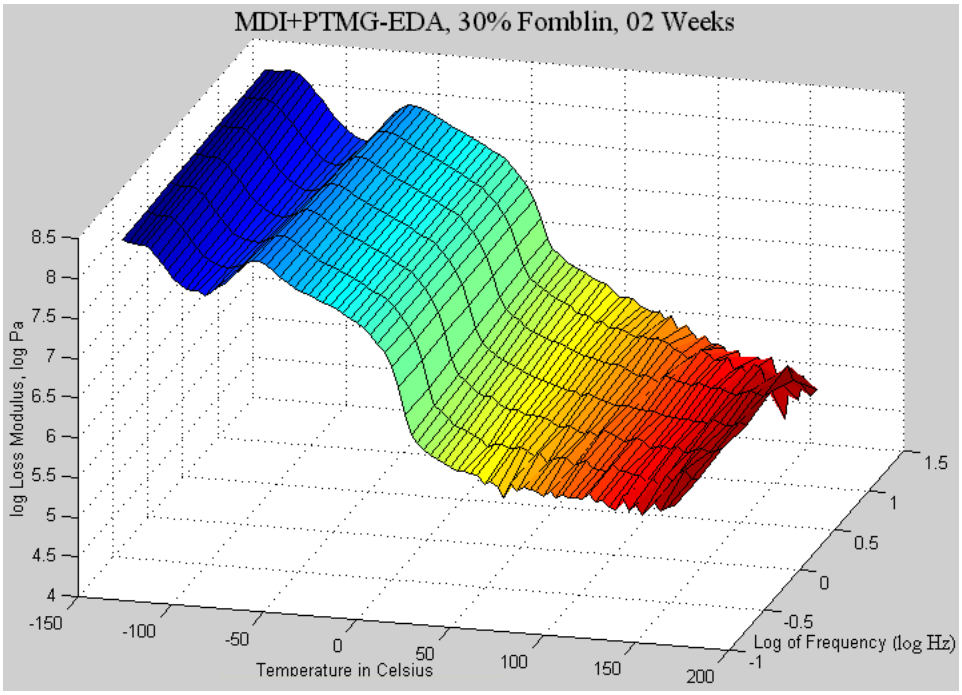

Figure C.35. PTMG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

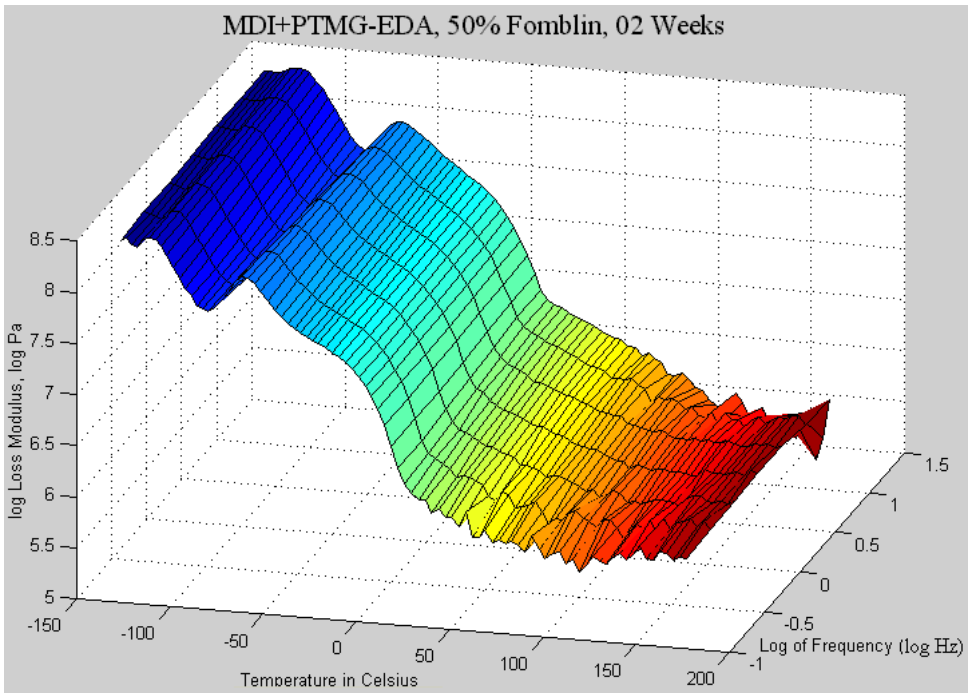

Figure C.36. PTMG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

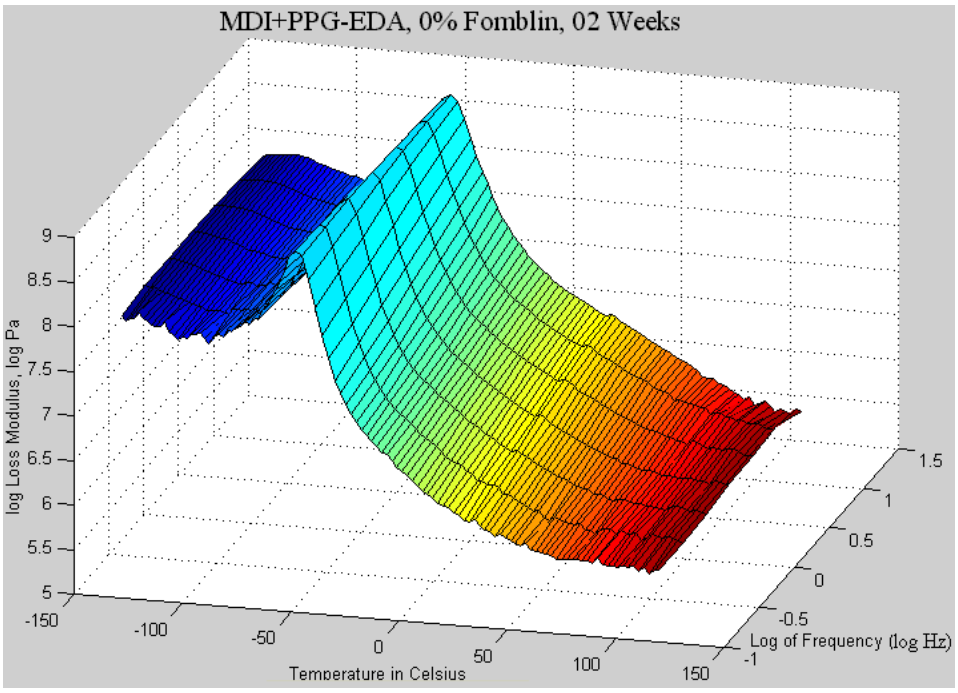

Figure C.37. PPG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

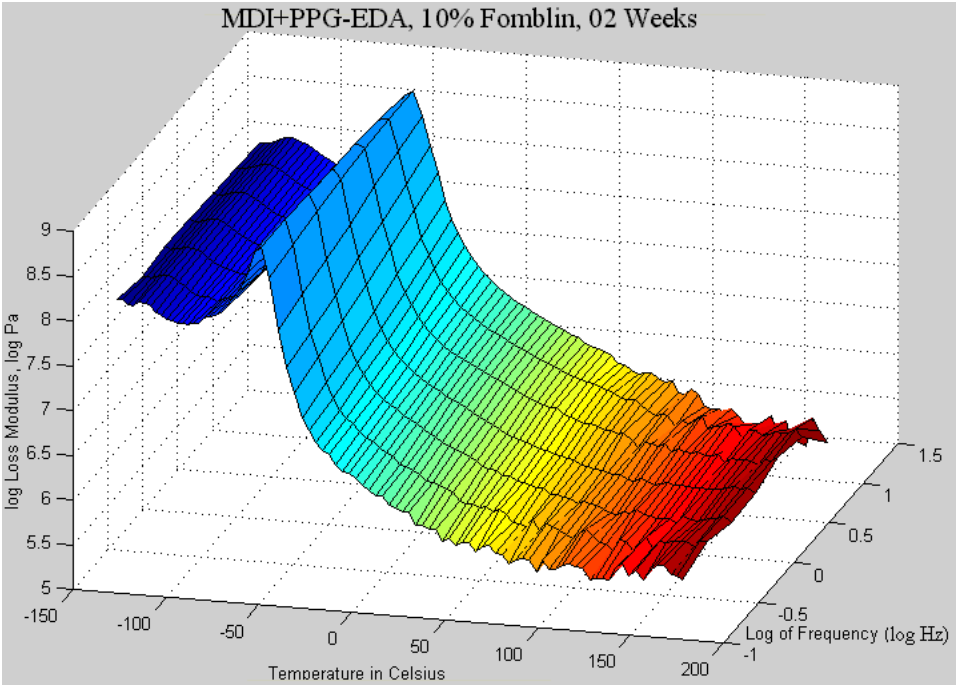

Figure C.38. PPG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

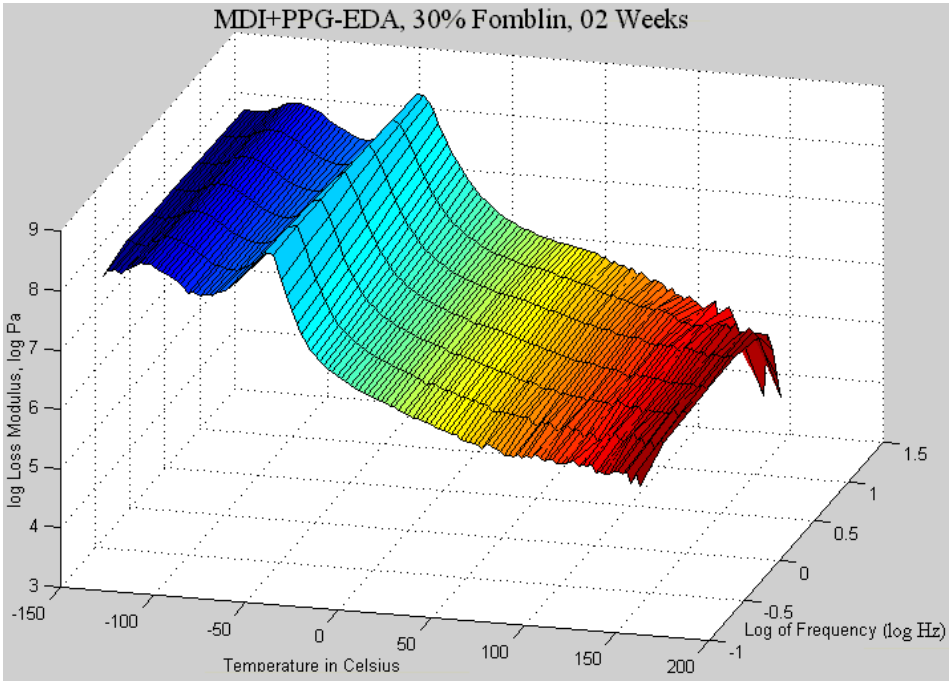

Figure C.39. PPG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

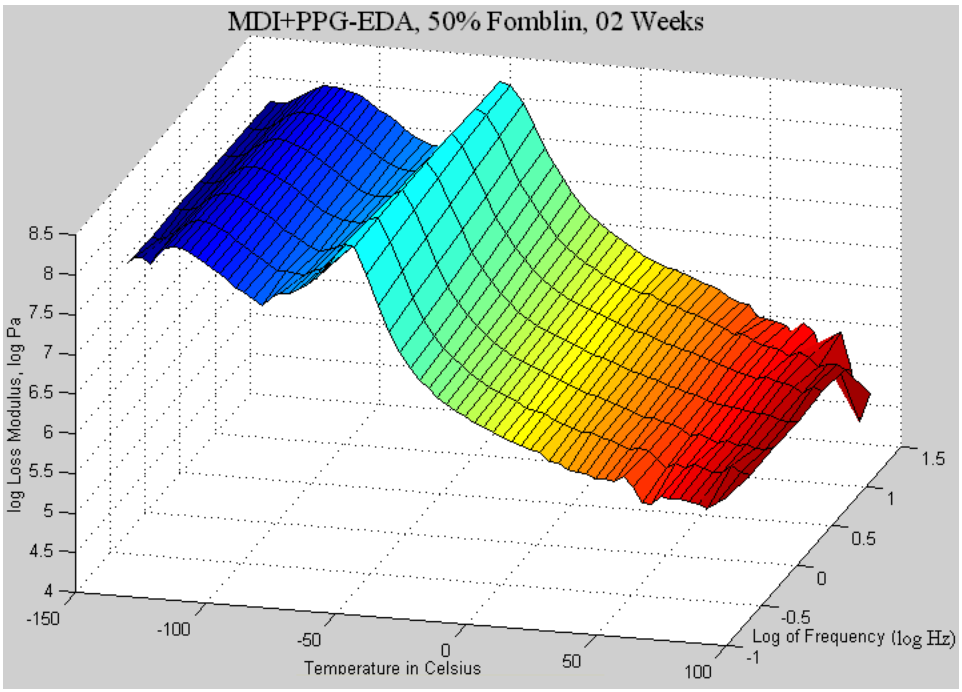

Figure C.40. PPG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, loss modulus versus temperature.

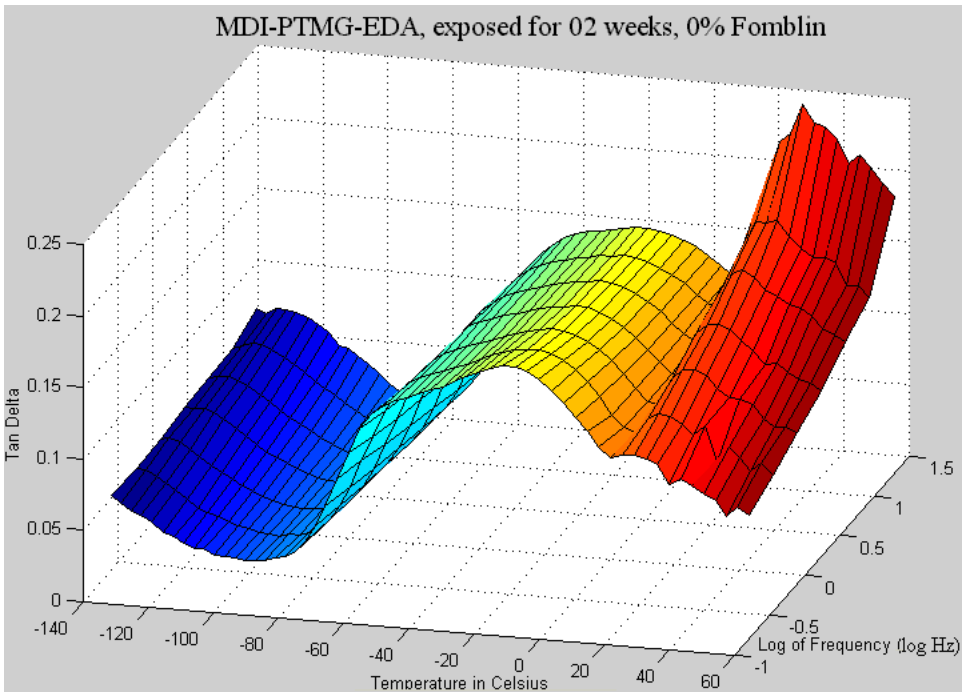

Figure C.41. PTMG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

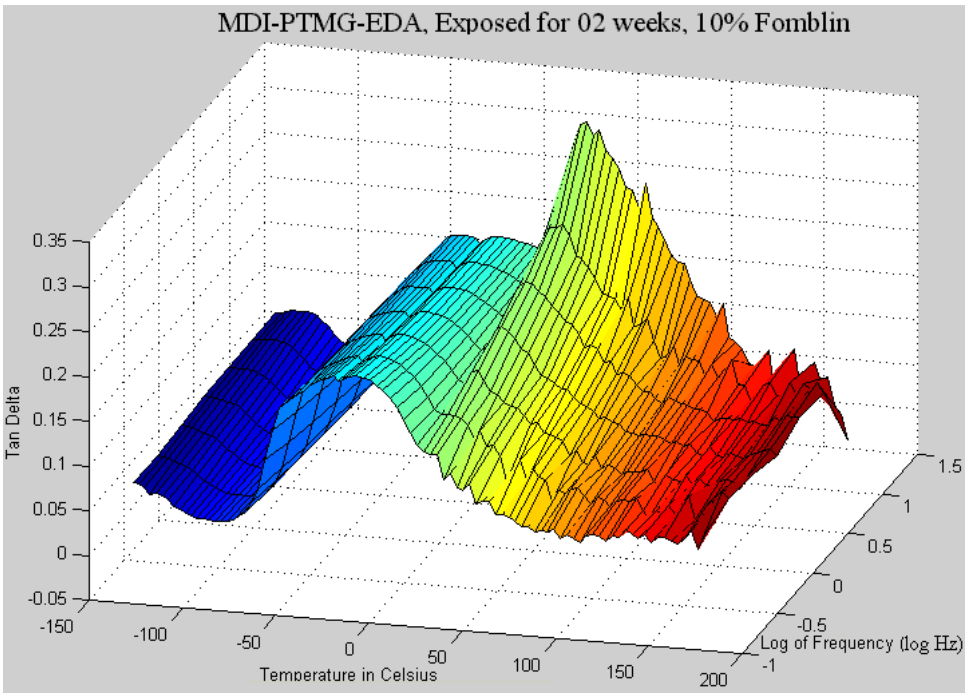

Figure C.42. PTMG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

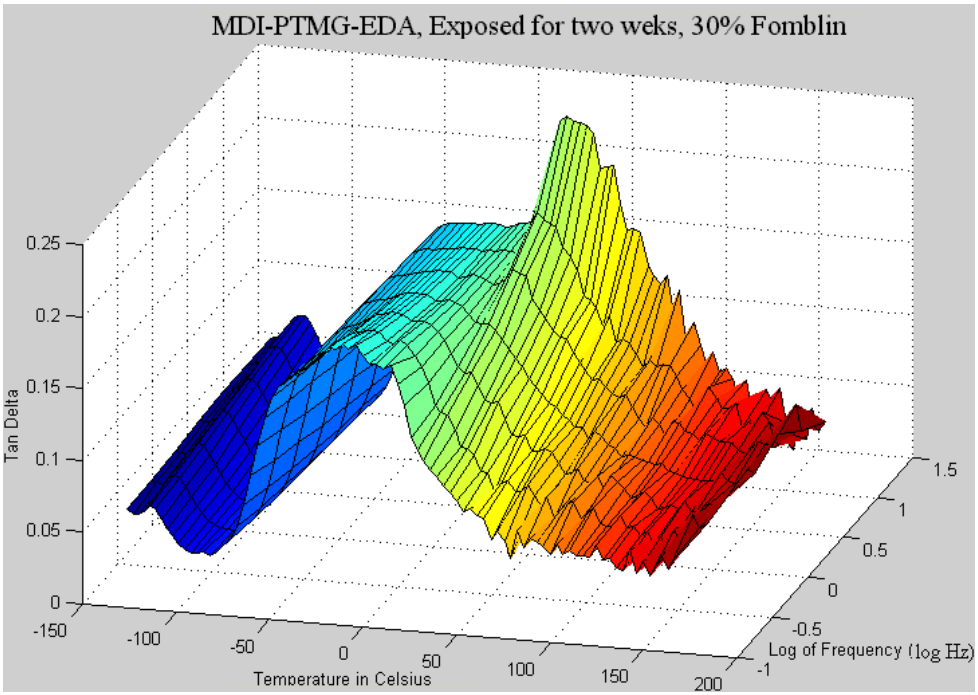

Figure C.43. PTMG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

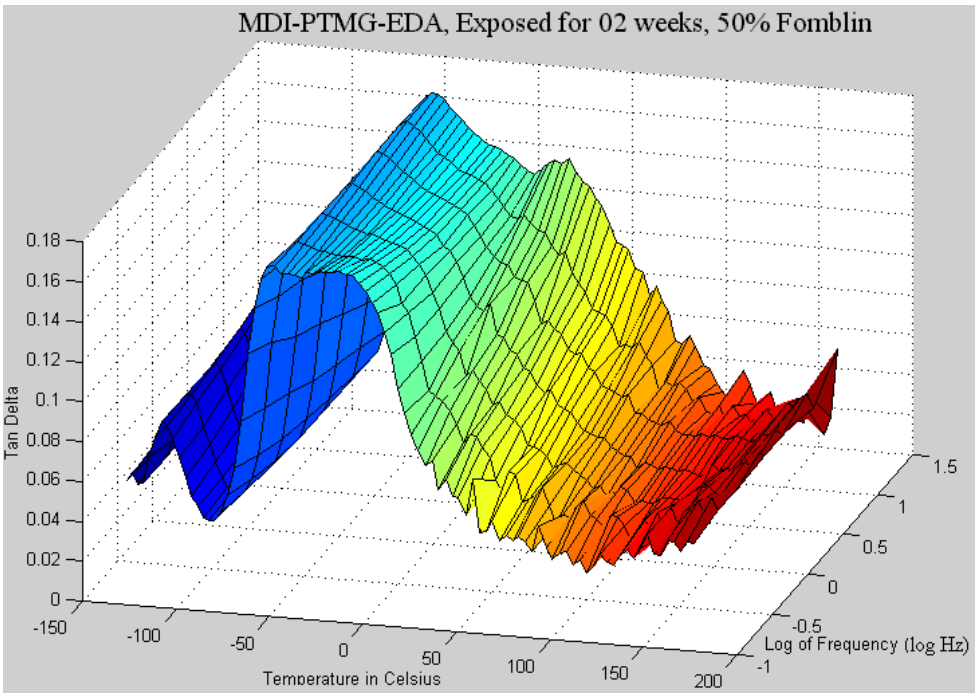

Figure C.44. PTMG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

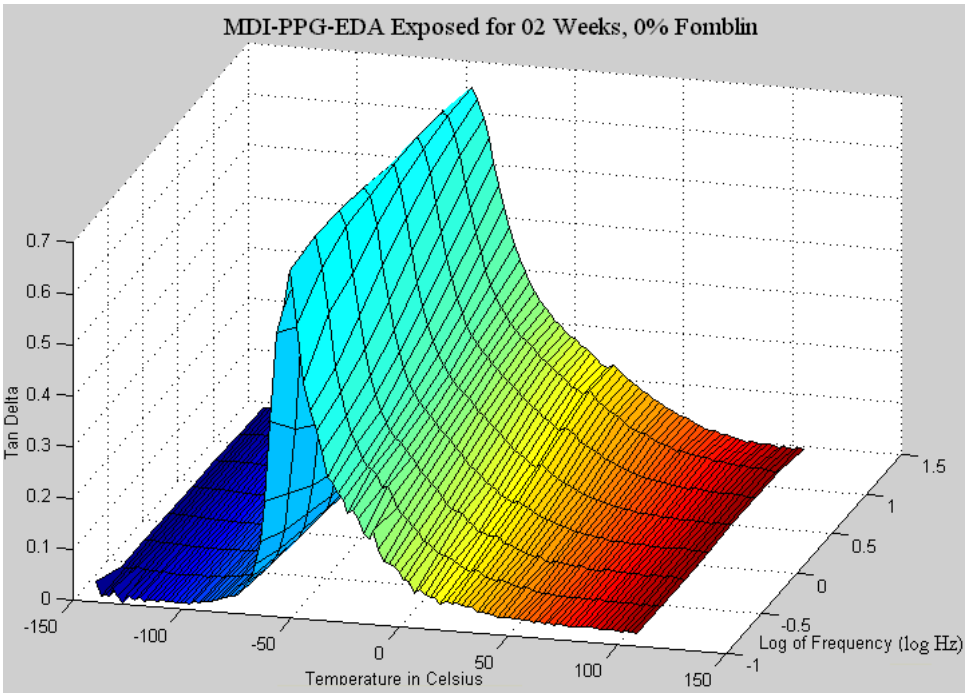

Figure C.45. PPG based PU, non-fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

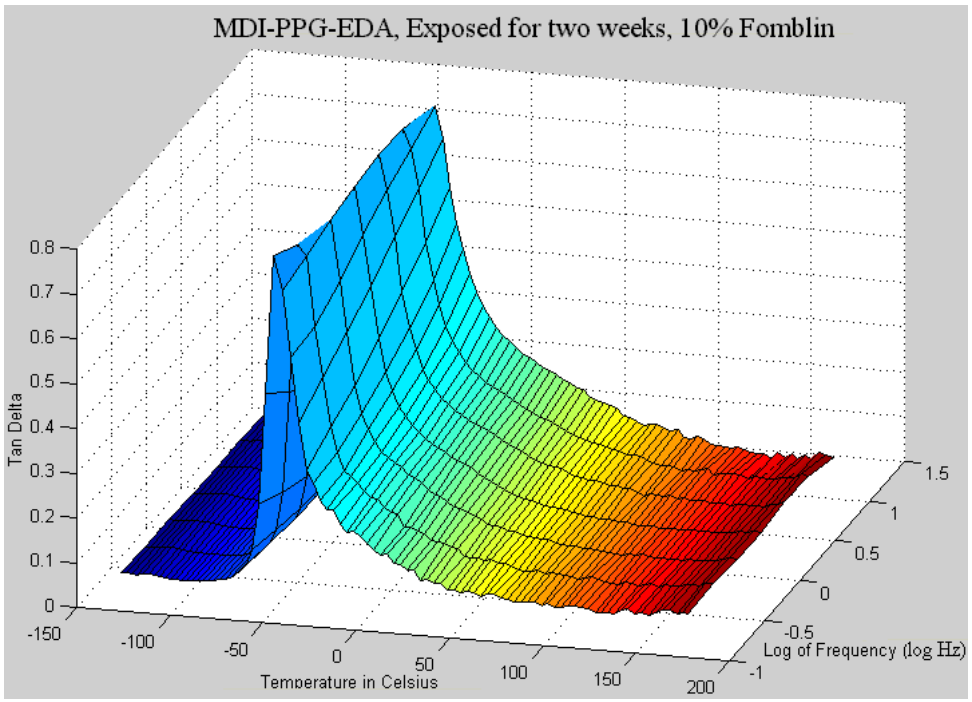

Figure C.46. PPG based PU, 10% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

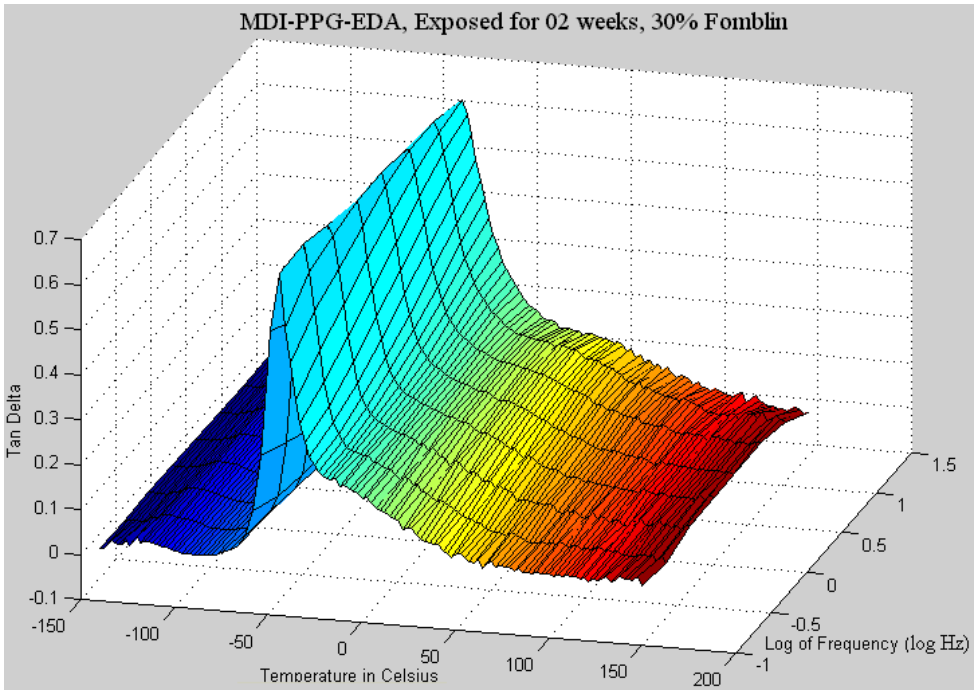

Figure C.47. PPG based PU, 30% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

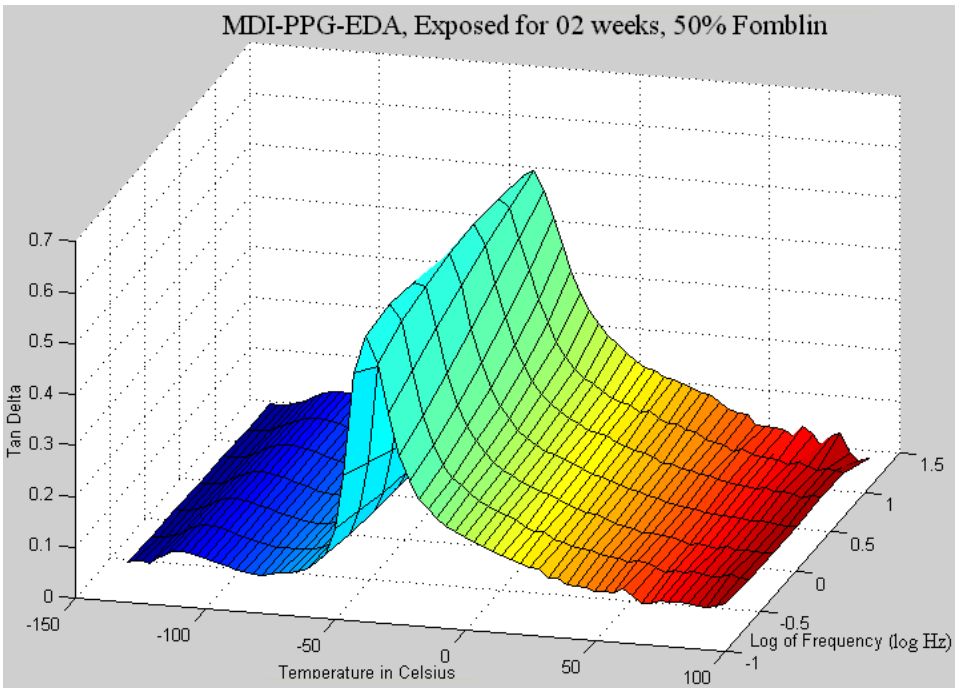

Figure C.48. PPG based PU, 50% fluorinated, exposed for 02 weeks at 118±3°C, Tanδ versus temperature.

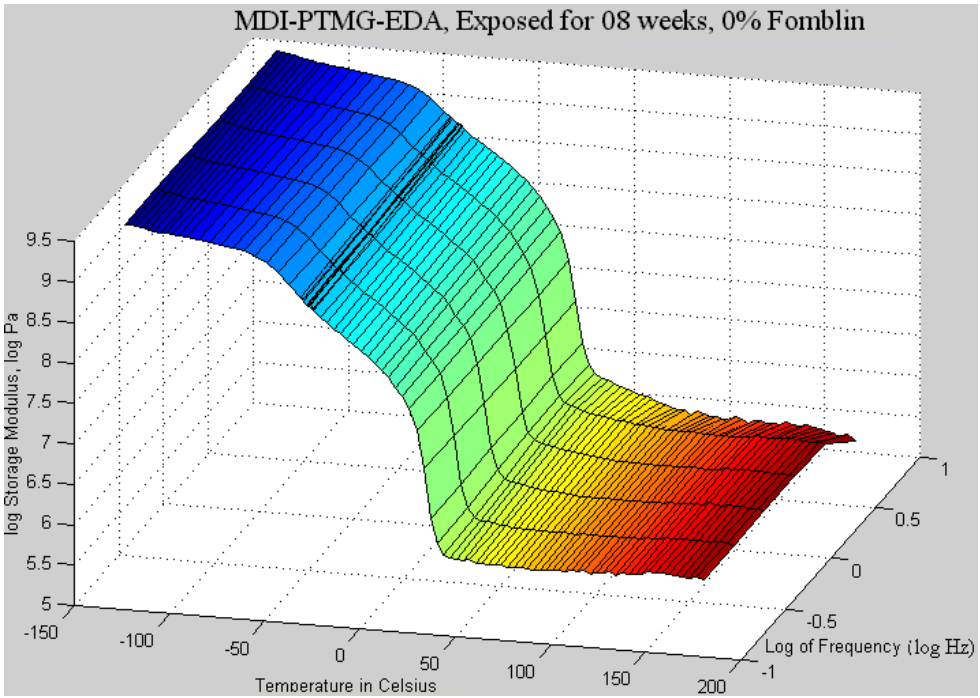

Figure C.49. PTMG based PU, non-fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

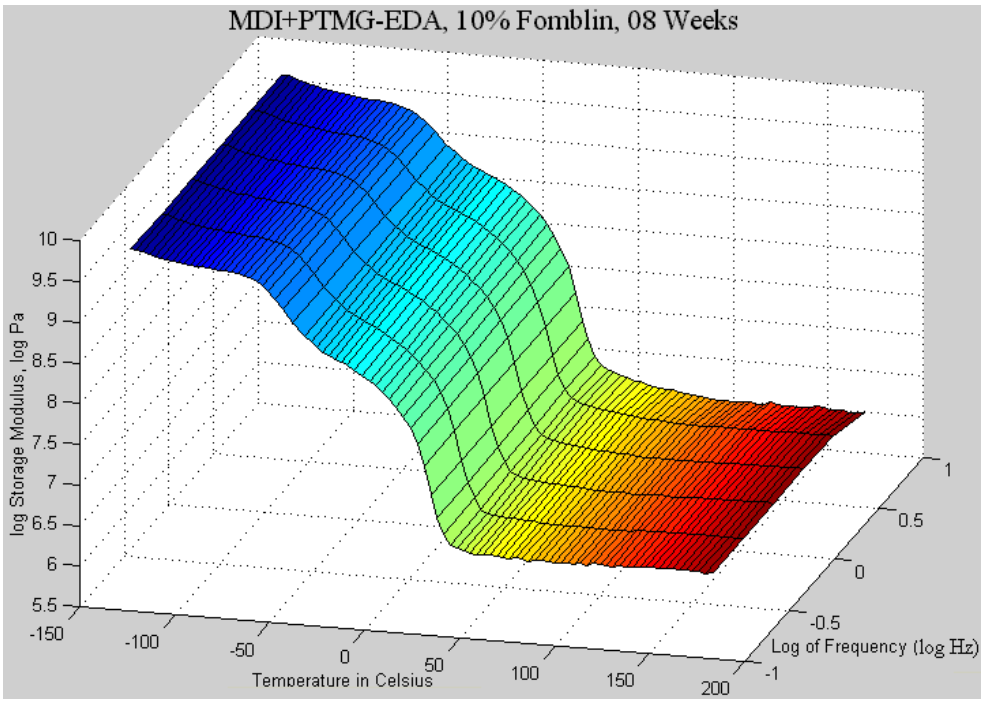

Figure C.50. PTMG based PU, 10% fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

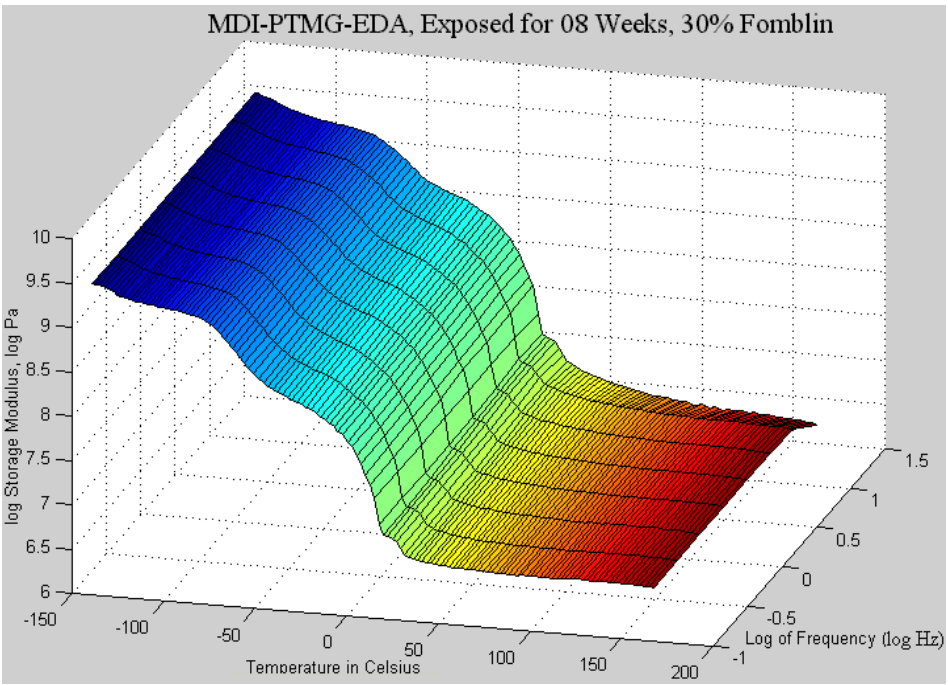

Figure C.51. PTMG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

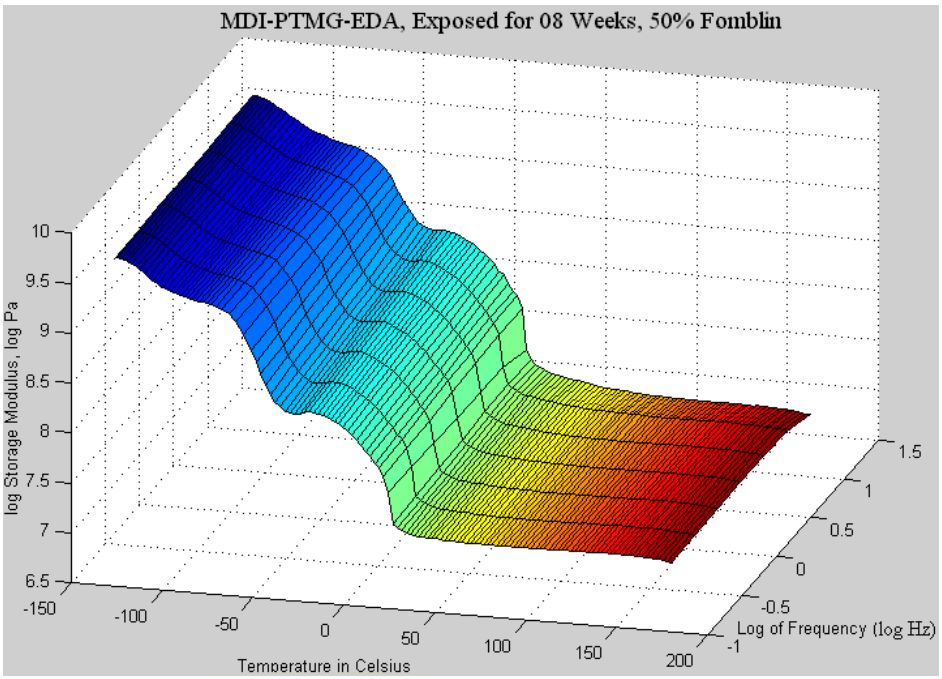

Figure C.52. PTMG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

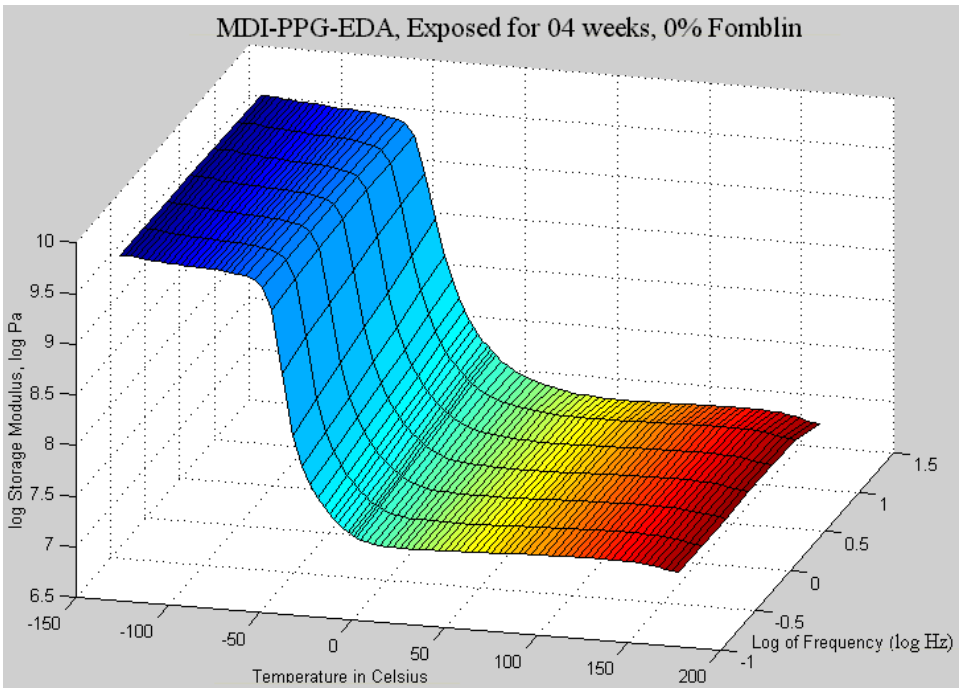

Figure C.53. PPG based PU, non-fluorinated, exposed for 04 weeks at 118±3°C, storage modulus versus temperature.

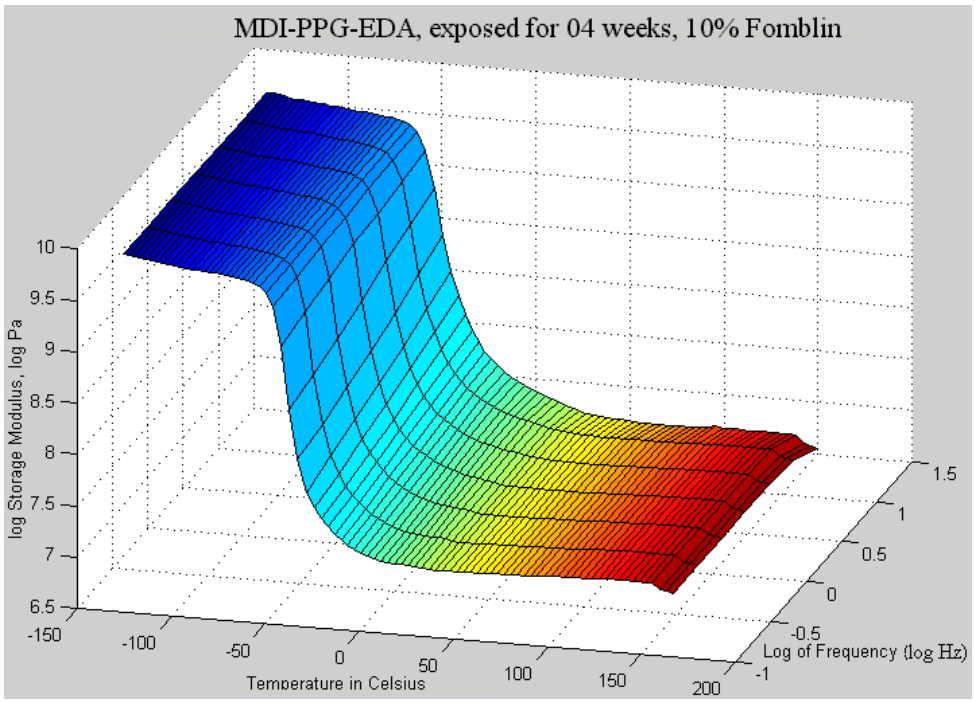

Figure C.54. PPG based PU, 10% fluorinated, exposed for 04 weeks at 118±3°C, storage modulus versus temperature.

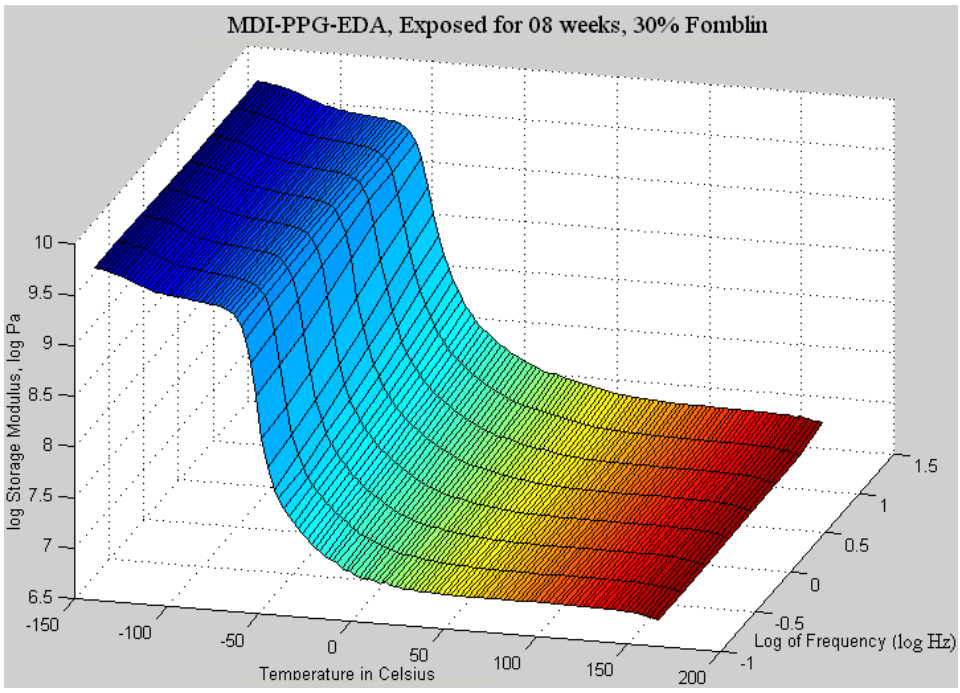

Figure C.55. PPG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

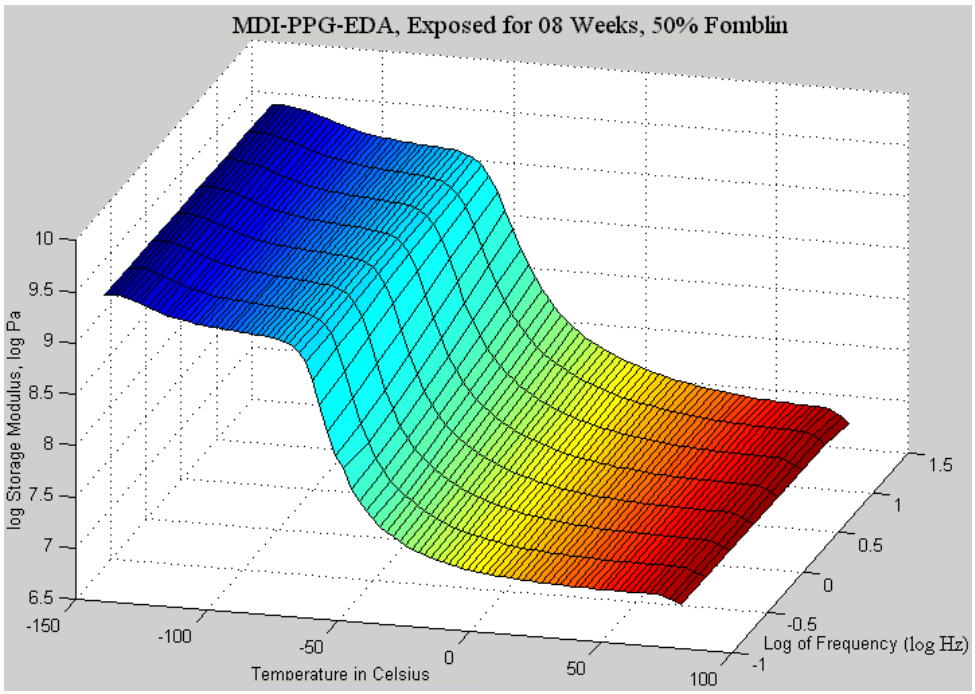

Figure C.56. PPG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, storage modulus versus temperature.

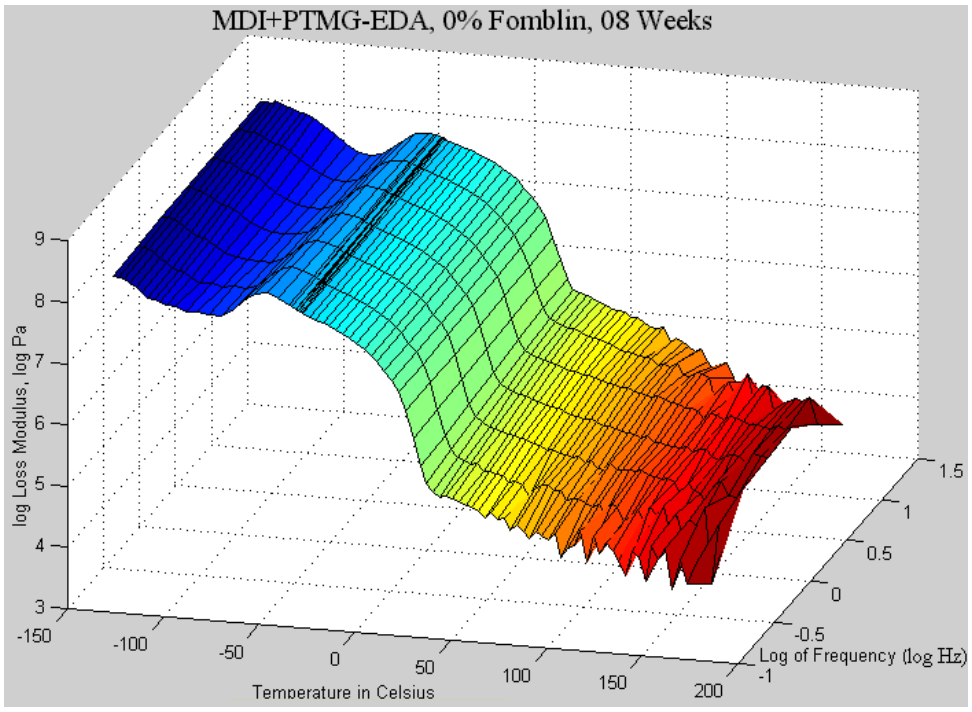

Figure C.57. PTMG based PU, non-fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

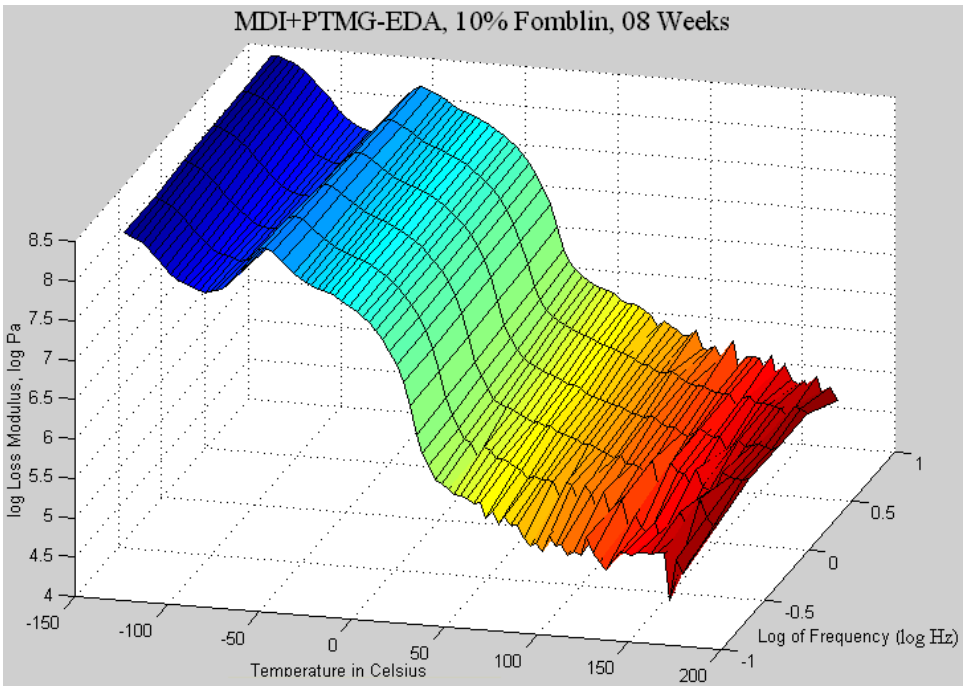

Figure C.58. PTMG based PU, 10% fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

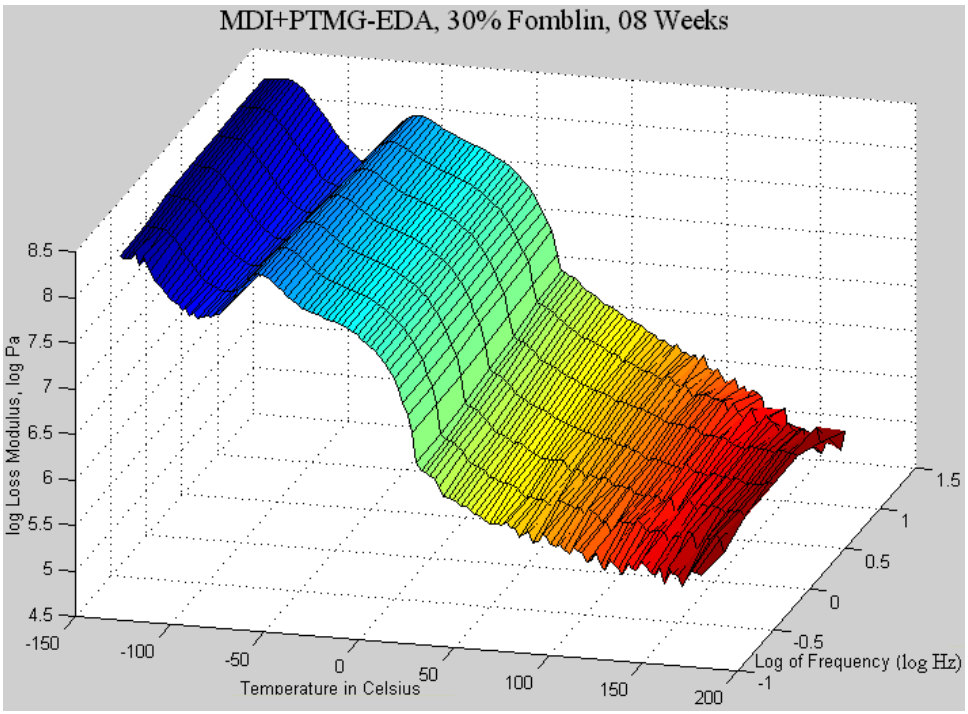

Figure C.59. PTMG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

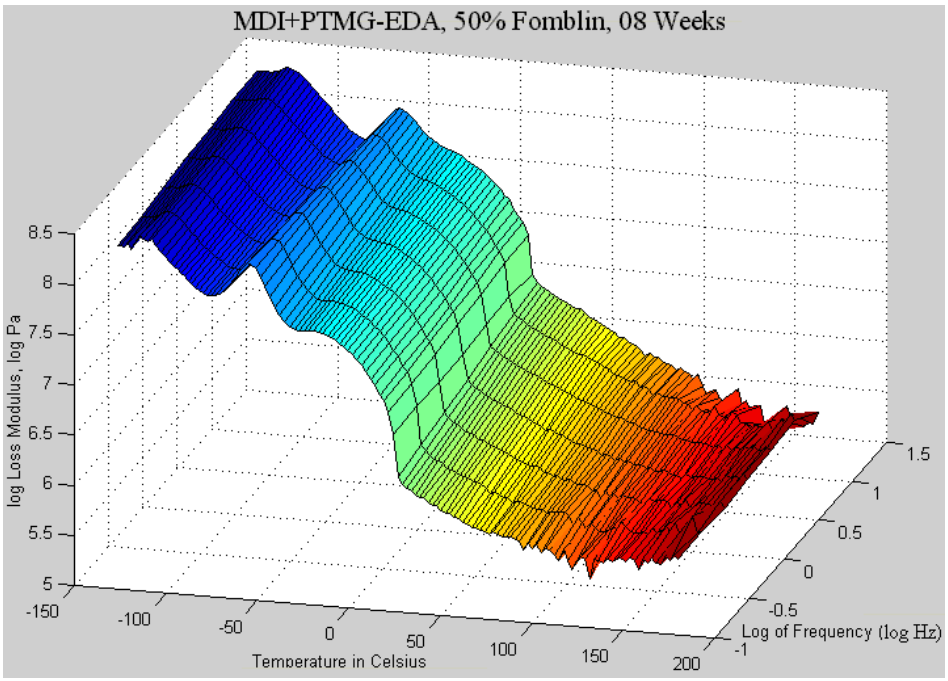

Figure C.60. PTMG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

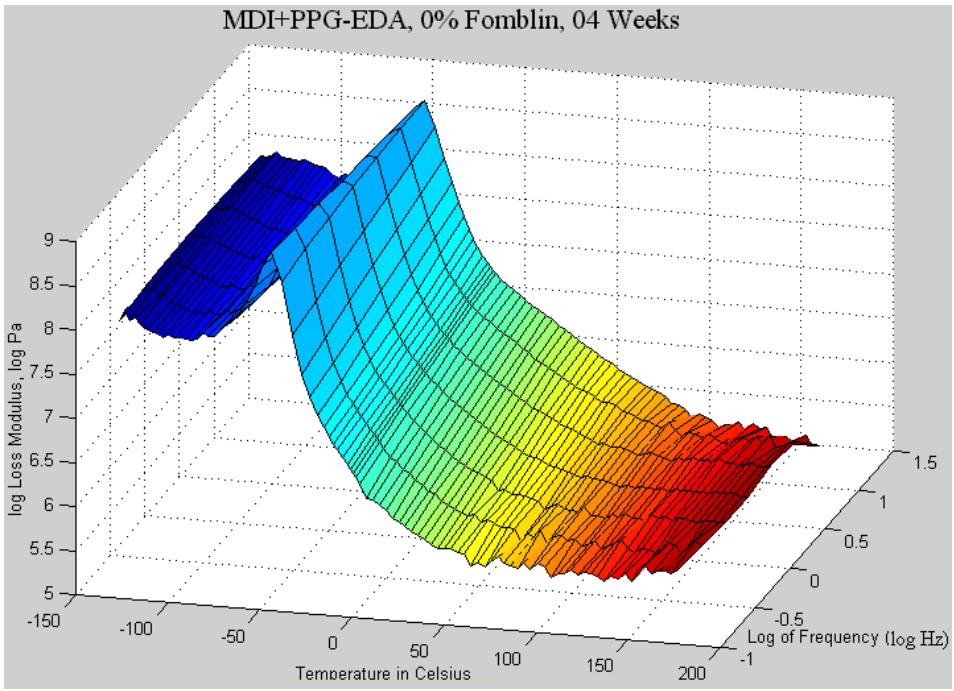

Figure C.61. PPG based PU, non-fluorinated, exposed for 04 weeks at 118±3°C, loss modulus versus temperature.

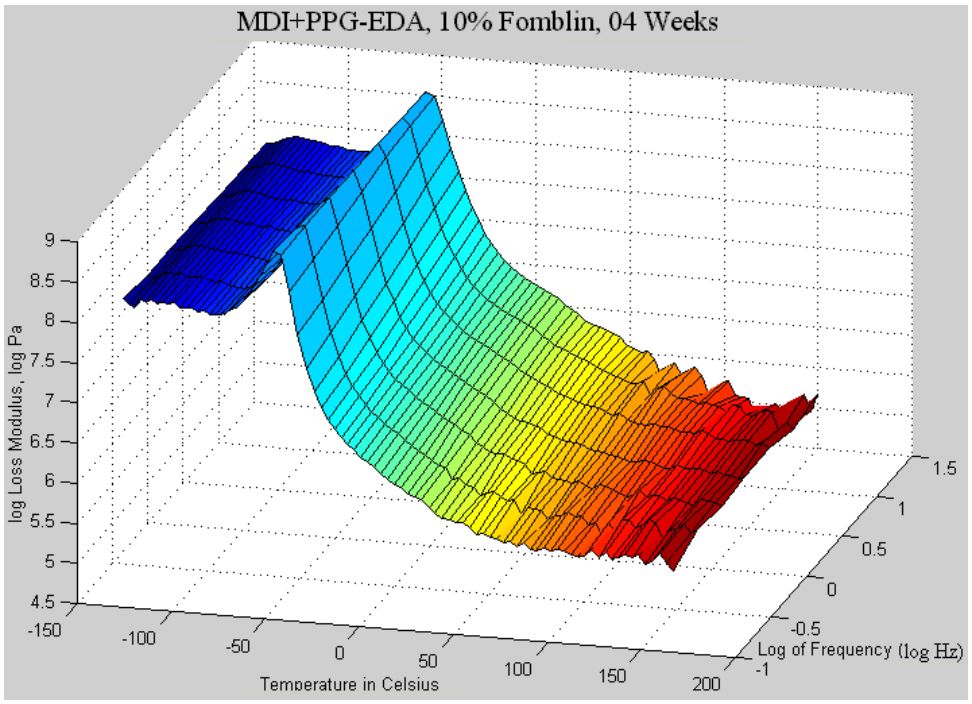

Figure C.62. PPG based PU, 10% fluorinated, exposed for 04 weeks at 118±3°C, loss modulus versus temperature.

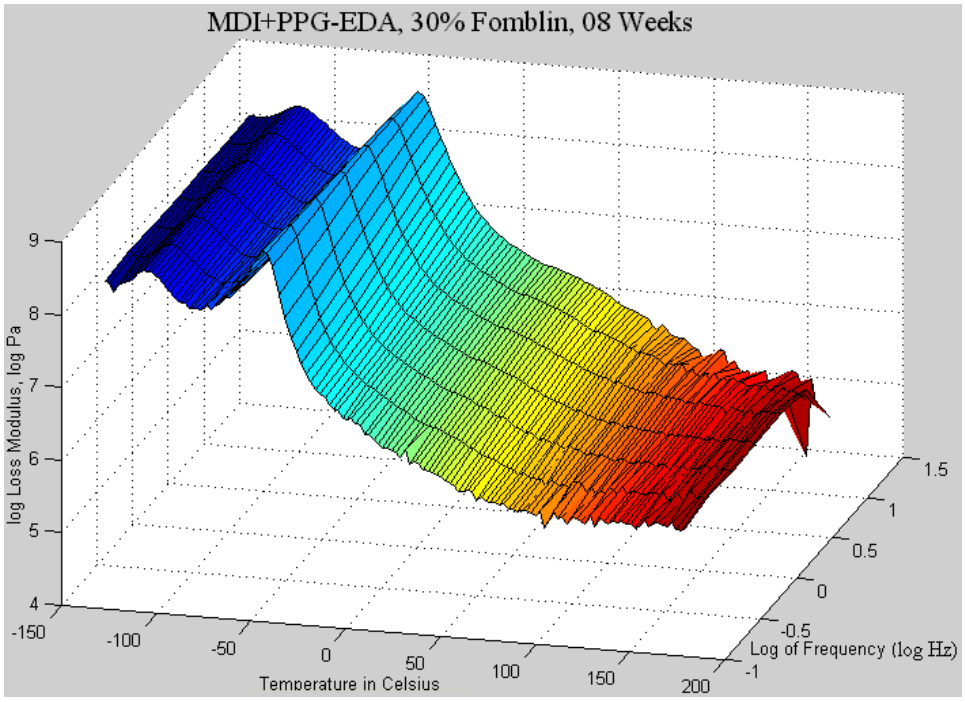

Figure C.63. PPG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

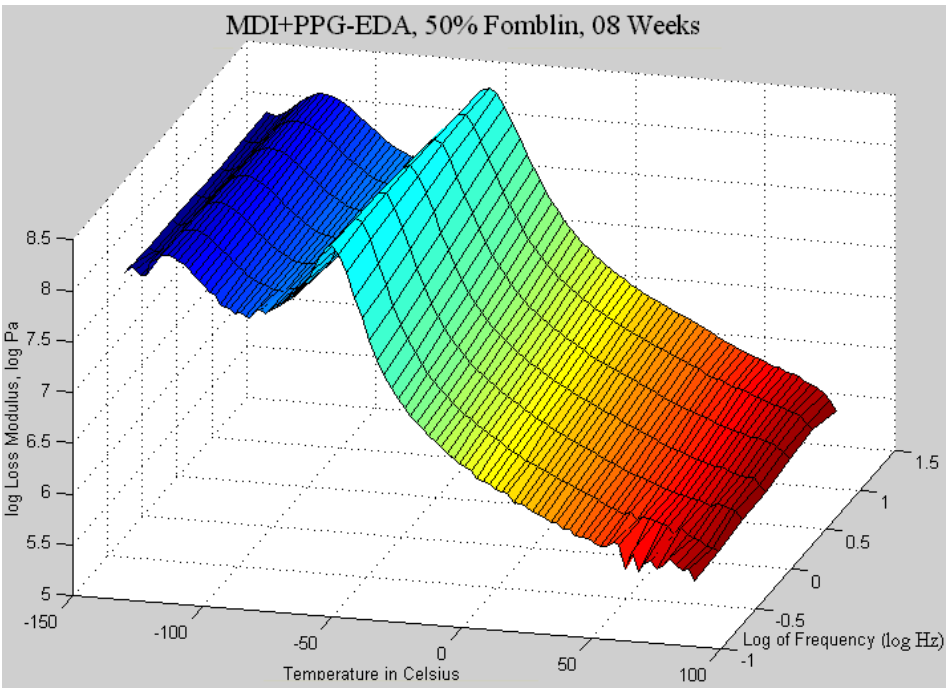

Figure C.64. PPG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, loss modulus versus temperature.

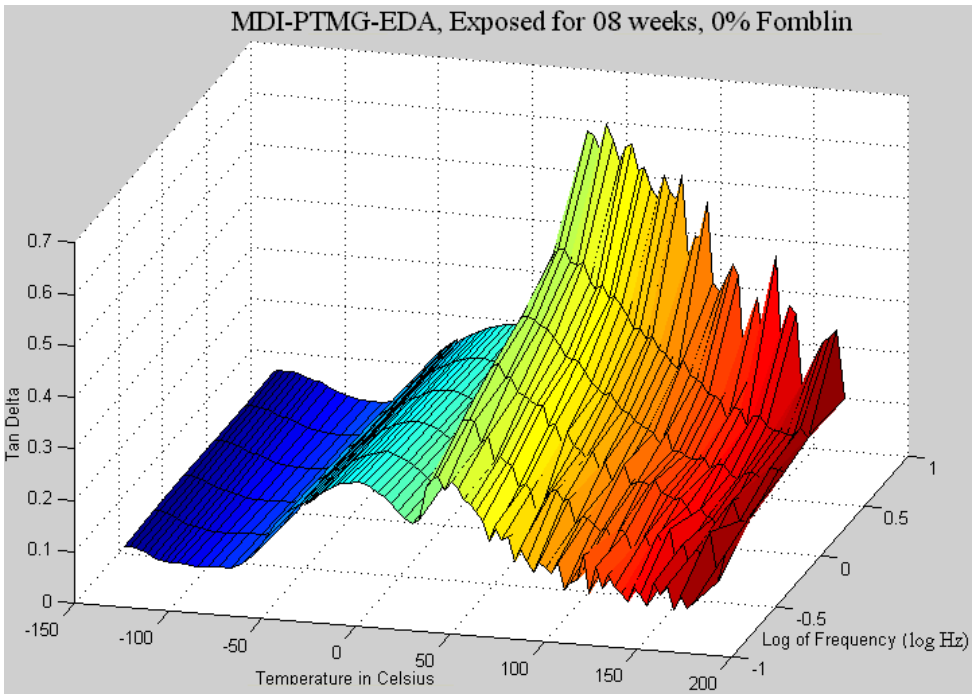

Figure C.65. PTMG based PU, non-fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

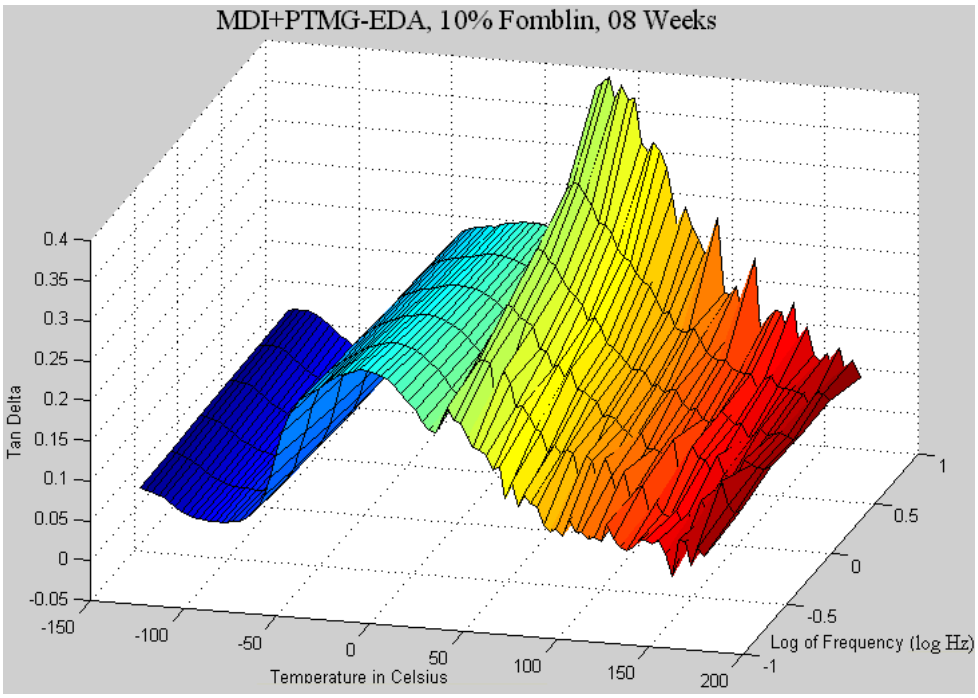

Figure C.66. PTMG based PU, 10% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

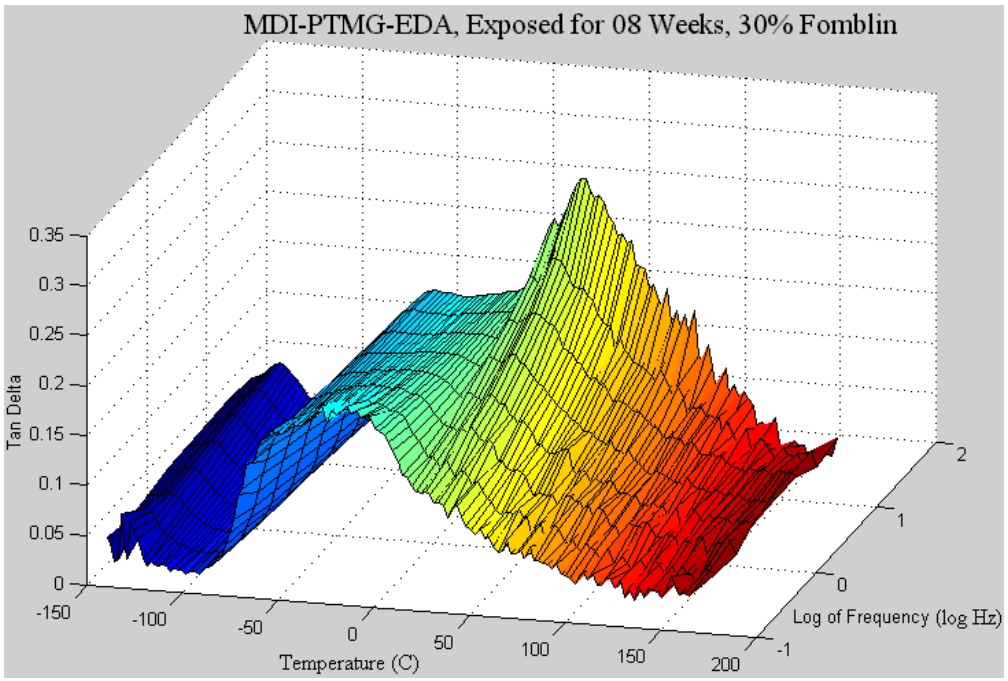

Figure C.67. PTMG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

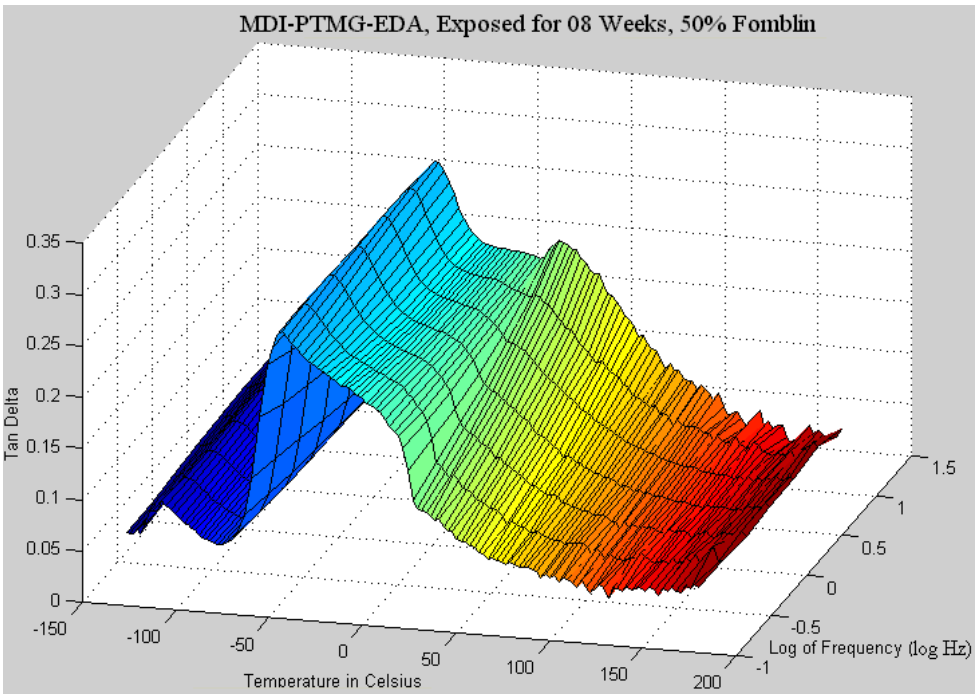

Figure C.68. PTMG based PU, 50% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

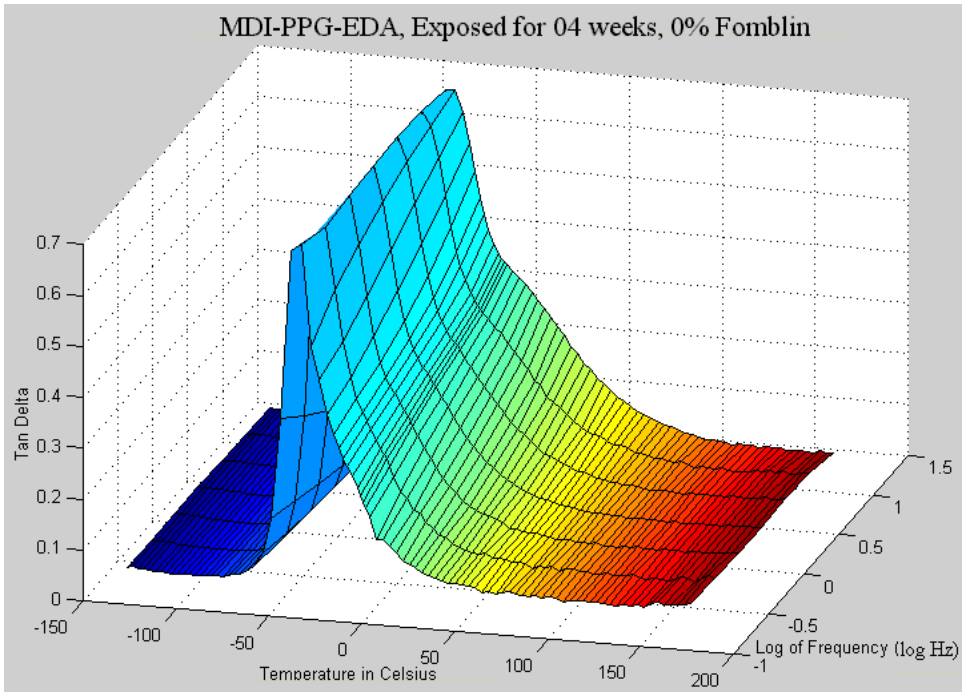

Figure C.69. PPG based PU, non-fluorinated, exposed for 04 weeks at 118±3°C, Tanδ versus temperature.

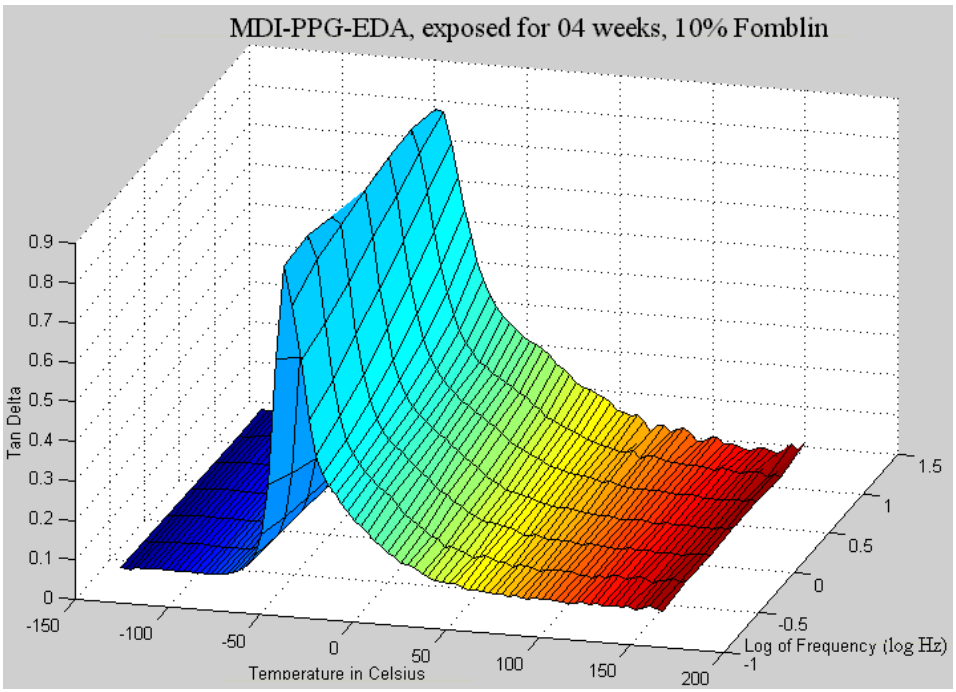

Figure C.70. PPG based PU, 10% fluorinated, exposed for 04 weeks at 118±3°C, Tanδ versus temperature.

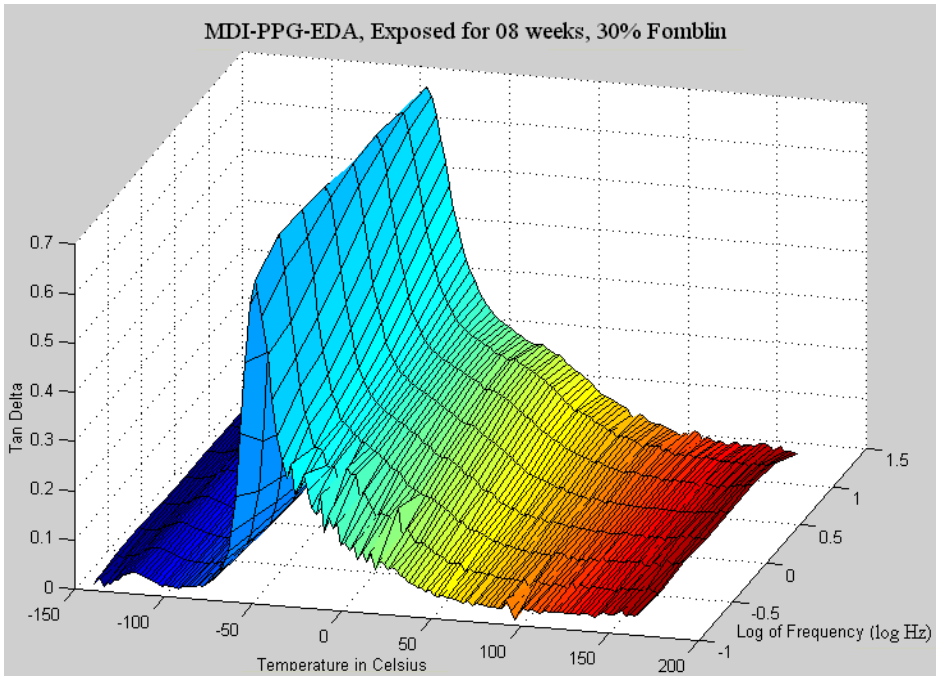

Figure C.71. PPG based PU, 30% fluorinated, exposed for 08 weeks at 118±3°C, Tanδ versus temperature.

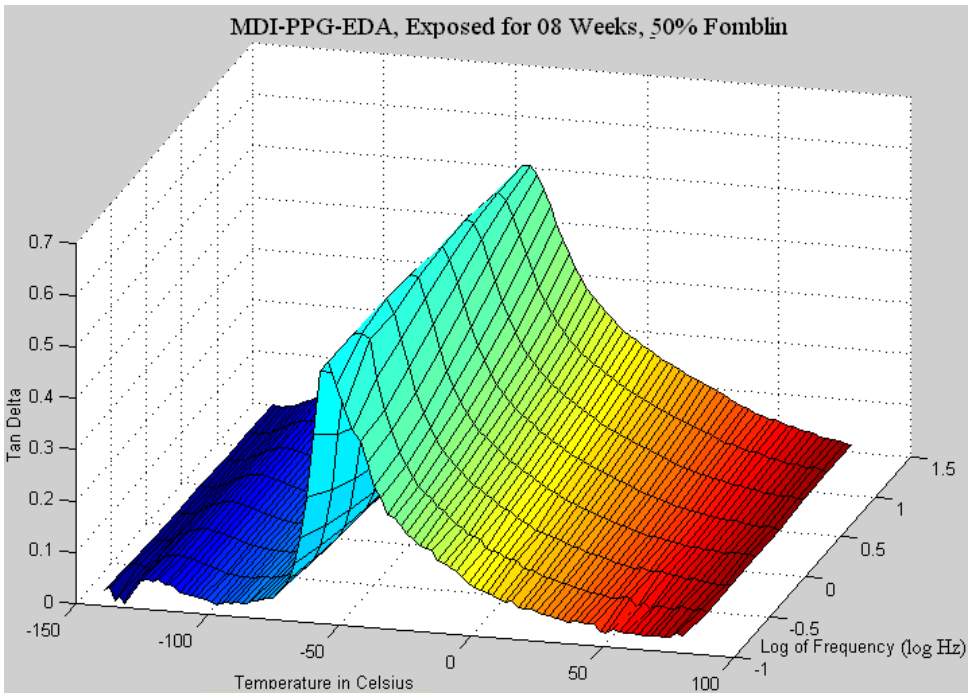

Figure C.72. PPG based PU, 50% fluorinated, exposed for 08 weeks at 118±3^{o}C, Tanδ versus temperature.

Appendix D: Matlab® code

dmaplots.m - Notepad

File Edit Search Help

```
%This matlab program was made for the default imaging of the DMA testing of my samples.
%Rogerio Silva Tocchetto, March 25th, 2002.

disp('This program will make 3D plots of the Tan delta and Storage Modulus')
disp('   ');
disp('Now input the matrix for the x values, the Temperature in Celsius, in between brackets')
disp('   ');
x=input(' ');
disp('Now input the matrix for the y values, the log of frequency, in between brackets')
y=input(' ');
disp('Now input the matrix for the z values, the Tan Delta, in between brackets')
z=input(' ');
disp('Now input the matrix for the Z values, the Storage Modulus, in between brackets')
Z=input(' ');

figure
surf(x,y,z,x);
view(15,30);
xlabel('Temperature in Celsius');
ylabel('Log of Frequency (log Hz)');
zlabel('Tan Delta');

disp('press any key to continue');
pause

figure
surf(x,y,Z,x);
view(15,30);
xlabel('Temperature in Celsius');
ylabel('Log of Frequency (Log Hz)');
zlabel('log Storage Modulus, log Pa');

disp('to make new plots, type clear and start over')
```

Figure D.1. Matlab® code designed for generating the DMA surface plots.

Appendix E: Activation energies obtained from DMA testing.

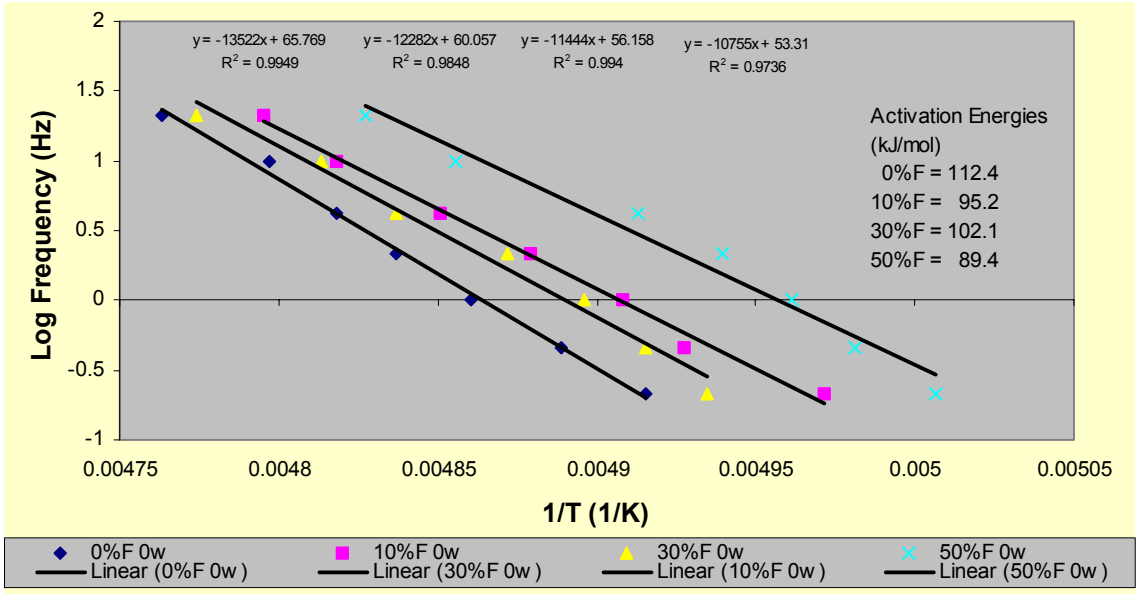

Figure E.1. Activation energies for the main transition of unexposed PTMG based polymers.

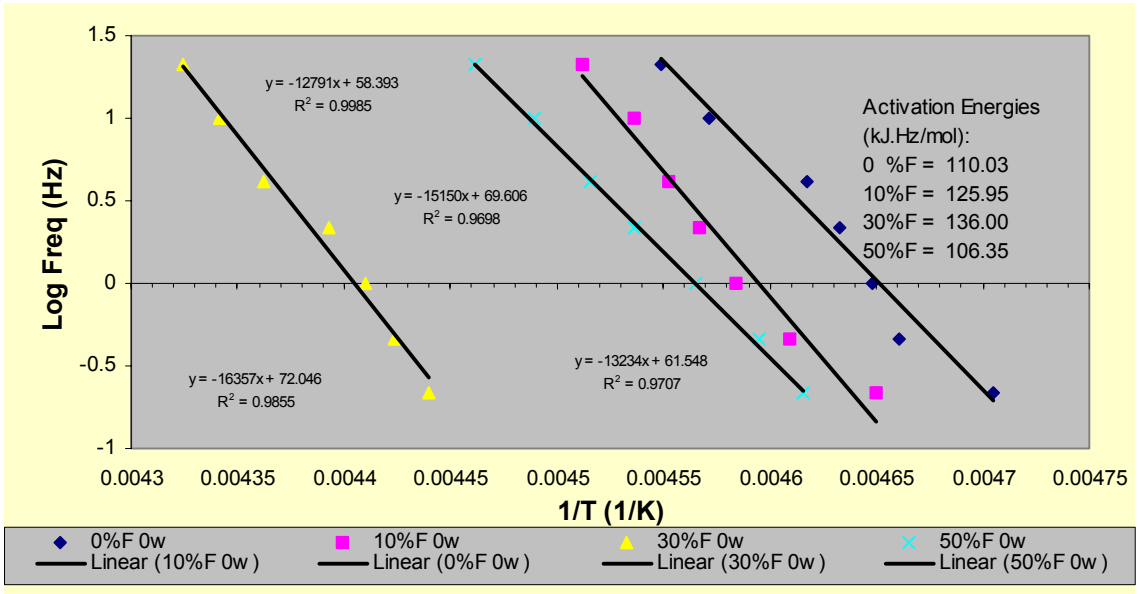

Figure E.2. Activation energies for the main transition of unexposed PPG based polymers.

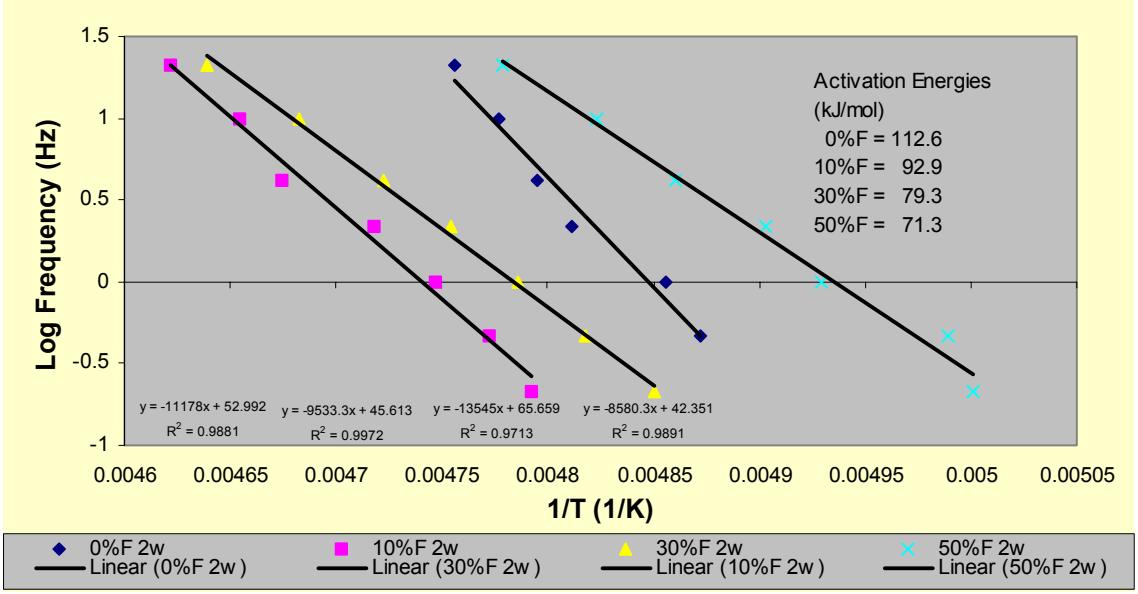

Figure E.3. Activation energies for the main transition of the PTMG based polymers exposed for 02 weeks.

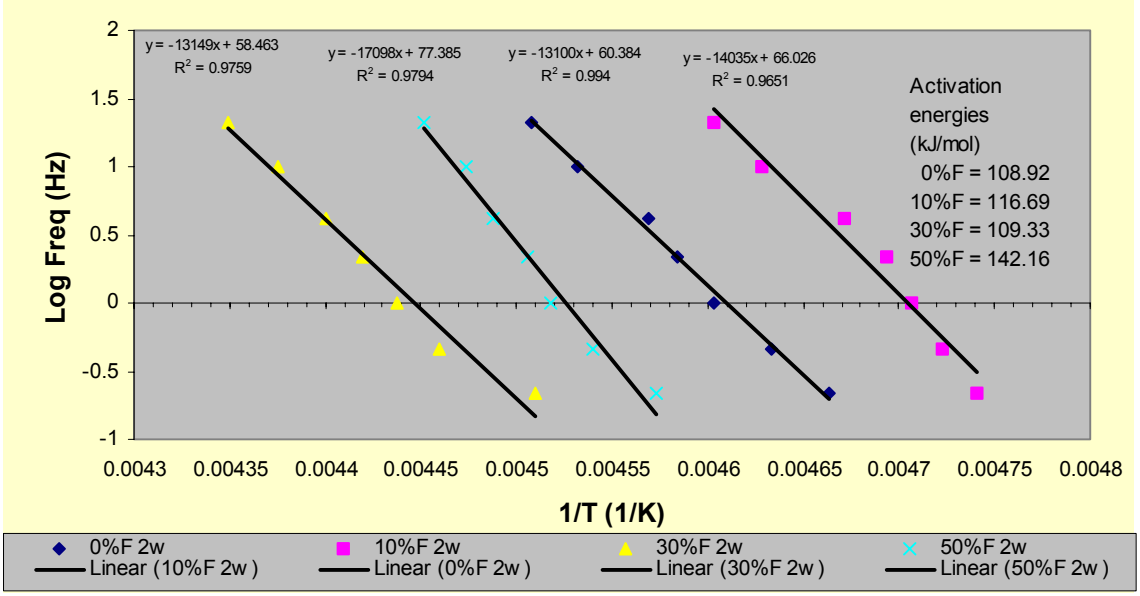

Figure E.4. Activation energies for the main transition of the PPG based polymers exposed for 02 weeks.

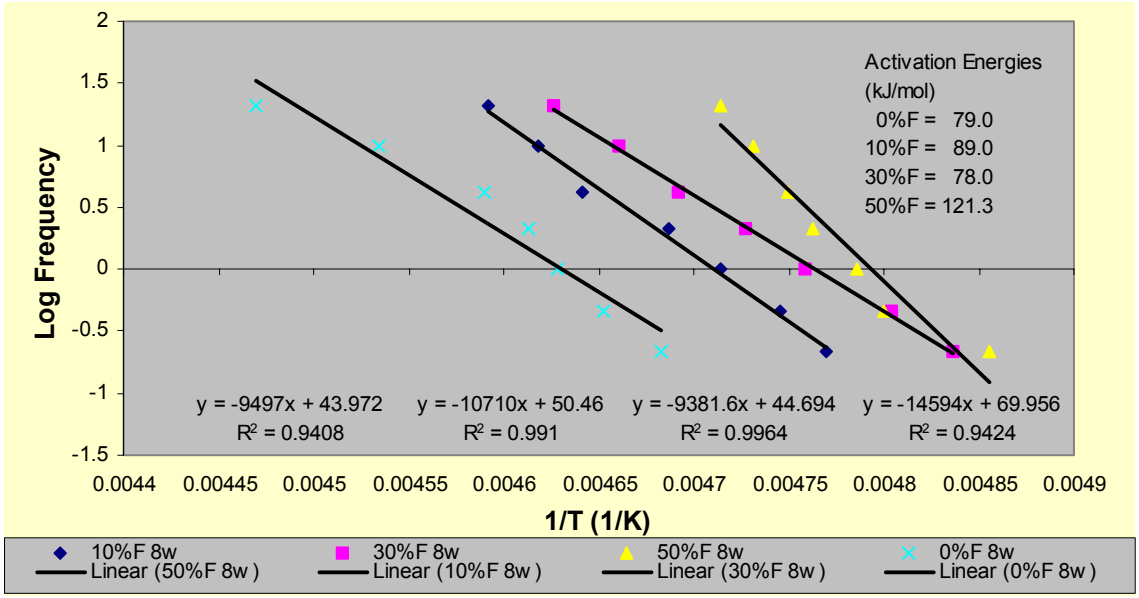

Figure E.5. Activation energies for the main transition of the PTMG based polymers exposed for 08 weeks.

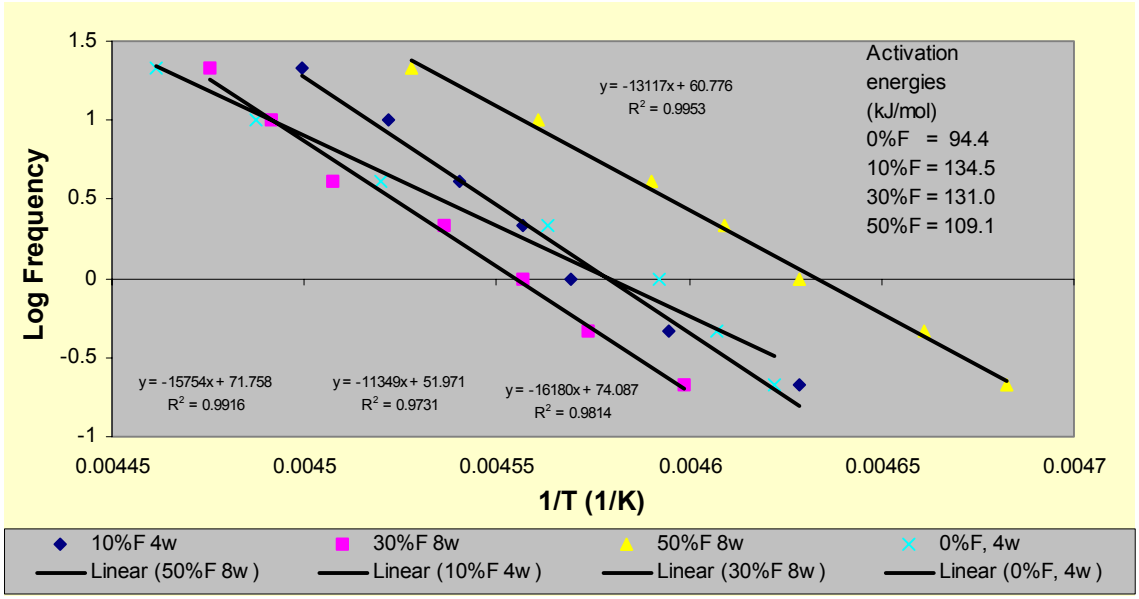

Figure E.6. Activation energies for the main transition of the PPG based polymers, final week of exposure.

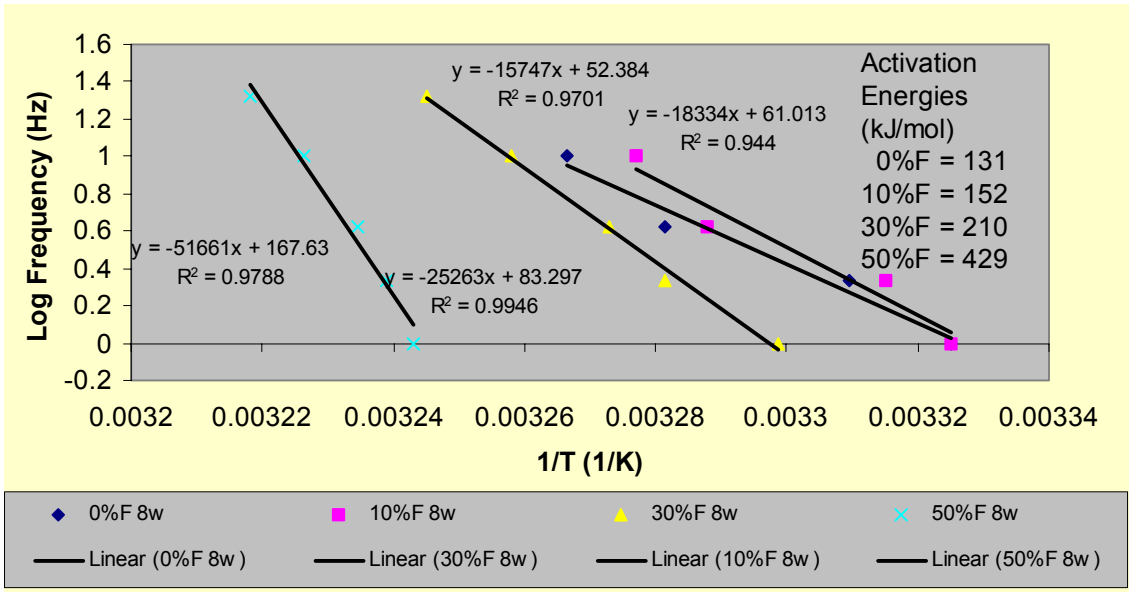

Figure E.7. Activation energies of the melting peak of PTMG based PUs exposed for 08 weeks. Activation energies with respect to Tanδ curves.

Appendix F: DSC results

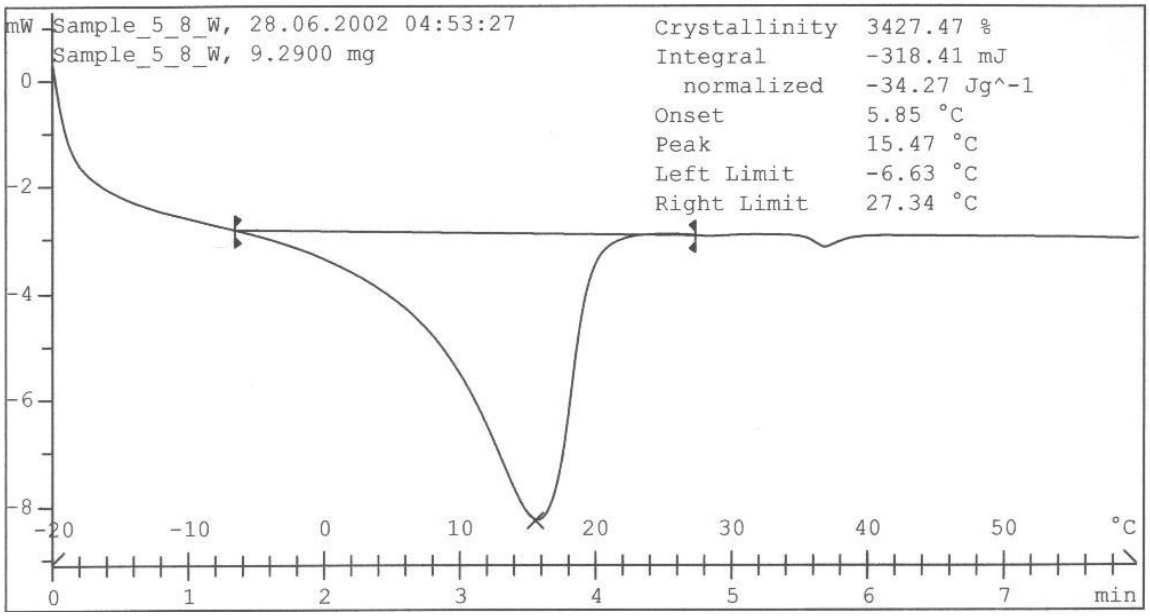

Figure F.1. MDI PTMG EDA non-fluorinated, exposed for eight weeks.

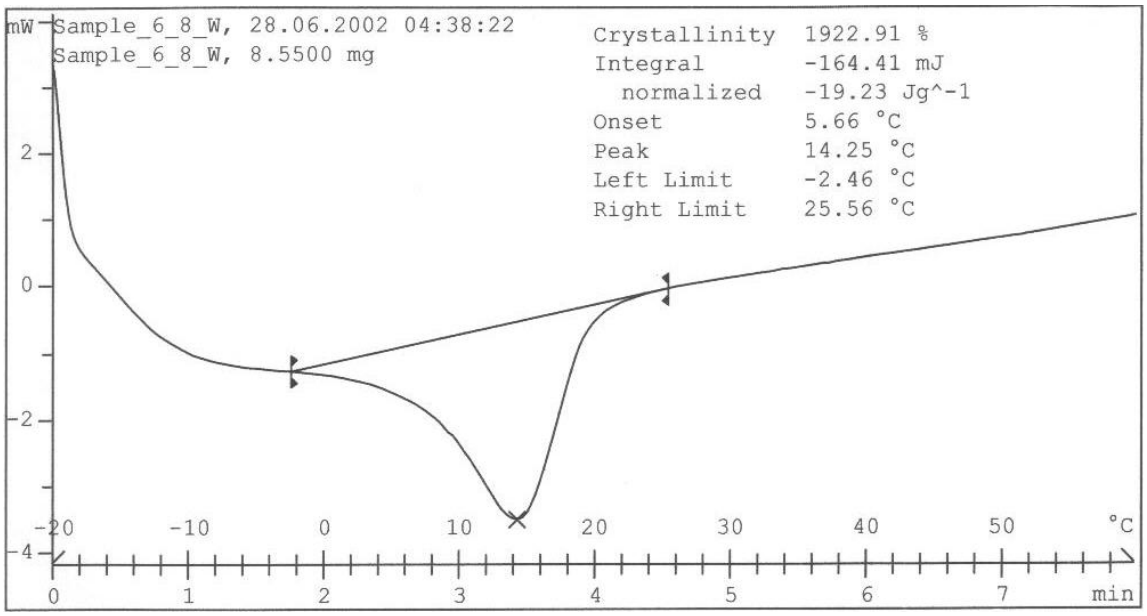

Figure F.2. MDI PPG EDA 10% fluorinated, exposed for eight weeks.

Vita

The author was born in Passo Fundo, southern Brazil on September 13th, 1975. He started his Bachelor in Materials Engineering in 1994 in Campina Grande, northeastern Brazil, graduating in 1999 with emphasis on Polymer Engineering. After brief industry related experience throughout his undergraduate program, he begun his graduate work towards his masters degree at The University of Tennessee Knoxville in the spring of 2000 under the guidance of Dr. Roberto S. Benson. During my higher education, works were published mainly in the field of degradation of polymers, including natural exposure of polypropylene based composites containing weld lines and biodegradable co-polyesters for mulching applications. The thesis research presented on this work continued the line of study in degradation of polymers. Studies in the field of the nucleation effect of talc in PP and pulltrusion of natural fibers composites were done during the undergraduate program, and UHMWPE composites wear studies (for knee implants) were done during the graduate program. He received his M.S. in the summer semester of 2002.